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16. ABSTRACT

This study was undertaken to decipher the mechanisms of solidification/-stabilization (S/S) of water soluble organics - namely phenol and ethylene glycol. Portland cement Type I was the binder used in ratios that varied from 2% to 50% organics/waste mixture. The S/S product was studied at various intervals using optical microscopy, scanning electron microscopy, x-ray power diffraction, energy dispersive elemental analysis, transmission electron microscopy and several physical tests.

The organics are not effectively immobilized toward water leaching. Effects on the matrix are very concentration dependent and are much more dramatic with ethylene glycol than with phenols. Although there is evidence of chemical reaction between the phenols and the fixing agents, the reaction does not result in chemical fixation of the organic.

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MORPHOLOGY AND MICROCHEMISTRY OF SOLIDIFIED/STABILIZED HAZARDOUS WASTE SYSTEMS

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency (U.S. EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the U.S. EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

Disposal of hazardous waste in landfills without pretreatment is known to be harmful to the environment in general, and to underground water specifically. Solidification/Stabilization of such waste to immobilize the toxic constituents is generally recognized as a viable treatment option. What is not clearly understood, however, is the mechanism of immobilization. Is it entrapment or is it chemical interaction with the binding agents? This study was conducted to seek answers to these questions. By understanding the mechanisms, custom designed solidification formulas can be developed for safe and effective treatment of hazardous waste. This report provides better insight into the nature of solidified mass on the micro and macro scale and how that changes with different interferences and at different levels. By understanding all of these factors, suitable management practices of hazardous waste can be achieved.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The aim of the present research is to gain information about the mechanisms by which solidification/stabilization schemes operate and to define the nature of the interferences associated with the presence of various classes of organic and inorganic compounds. Studies of water-soluble organics, including ethylene glycol and phenols, in Type I Portland cement have been carried out using leaching tests, physical tests and a variety of microscopic and spectroscopic techniques. The systems studied are now the most thoroughly characterized combinations of organics with cement pastes. None of the water-soluble organics are effectively immobilized, even though the phenols are converted to calcium salts, which are less soluble in water than the original phenol. The organics are responsible for substantial changes in the cement matrix itself. These changes have been identified, and further work will attempt to correlate the changes with increased or decreased effectiveness of immobilization. A somewhat surprising result is the relatively small changes in compressive strength which result from the inclusion of large amounts of phenols. The strength is maintained even though there are major changes in the morphologies of the cement phases and even the chemical nature of the phases. The presence of ethylene glycol, on the other hand, gives rise to a steadily decreasing compressive strength as additional glycol is added. Another surprising observation is the qualitative difference in the distribution pattern of p-bromophenol in the cement matrix compared to p-chlorophenol. The result demonstrates that even very subtle changes in chemical composition of the waste can result in major changes in immobilization mechanism and efficiency.

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ABBREVIATIONS

WES	Waterways Experiment Station of the U.S. Army Corps of Engineers
SEM	Scanning electron microscopy
XRD	Powder x-ray diffraction
EDXA	Energy dispersive x-ray analysis
EPMA	Electron probe microanalysis
TEM	Transmission electron microscopy
SAD	Selected area diffraction
pAMP	*p*-Aminomethylphenol
pBP	*p*-Bromophenol
pCP	*p*-Chlorophenol
EG	Ethylene glycol
DCM	Dichloromethane
DMSO	Dimethylsulfoxide
gc	Gas chromatography
EP Tox	Toxicity characteristic extraction procedure (Method 1310)
TCLP	Toxicity characteristic leaching procedure
TEA	Triethanolamine
C_3A	Tricalcium aluminate (cement clinker phase)
C_2S	Dicalcium silicate (cement clinker phase)
C_3S	Tricalcium silicate (cement clinker phase)
CH	Calcium hydroxide (hydrated cement phase)
CSH	Calcium silicate hydrate gel (hydrated cement phase)

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INTRODUCTION

Solidification/stabilization is a common technology used for immobilization of wastes prior to landfilling, roadbed construction, etc. The technology has been most commonly studied as a potential technique for immobilization of toxic metal ions or radioactive waste. Complete detoxification of metals by chemical, biological or other means is impossible short of elemental transformation; hence, methods which dilute and/or isolate the metals are necessary as part of waste management schemes. Many vendors of solidification/stabilization technology have presented leaching data claiming to show the efficacy of various immobilization techniques; although claims concerning the nature of chemical interactions between waste metal ions and fixing agents have remained unsubstantiated.[1]

The aim of the present research is to gain information about the mechanisms by which solidification/stabilization schemes operate and to define the nature of the interferences associated with the presence of various classes of compounds, both inorganic and organic. Conceptually, there are two broad classes of mechanism; namely, physical entrapment and chemical interaction. The present research is using a combination of physical tests, spectroscopy and microscopy to gain information about the interactions of various species with typical solidification/stabilization matrices.

The two principal constituents of most commercial fixing agents are cementitious materials (Portland cement, fly ash, etc.) and soluble silicates. A limitation often cited is that the processes are incompatible with organics, but details about the types of organics which interfere or the concentrations at which interference is detrimental are not available.[2] The same is true with many inorganic materials. A potential concern is that interferences, even in small amounts, can alter the process sufficiently to substantially decrease the ability of the fixing agents to immobilize metal ions. Indeed, it is well known that admixtures can alter the setting characteristics of Portland cement. It is not clear whether, and at what concentrations, various materials which are commonly present in waste streams interfere with the complex setting reactions resulting in a significantly altered cement matrix. The question is of obvious interest with respect to solidification/stabilization technology, since complex mixed inorganic/organic waste streams are commonly encountered.

RESEARCH GOALS AND METHODS

OBJECTIVES

The present research aims to produce the first thorough characterization of several examples of wastes solidified in a cement matrix. The initial part of the work, to be reported here, has concentrated on method development and on applications of the methods to model systems of pure, water-soluble organics in Type I Portland cement. We are looking for correlations of changes in cement matrix structure with the ability of the matrix to immobilize the organics, with the latter being measured by such properties as leachability and compressive strength. The ultimate goal of the research is to be able to predict incompatibilities of waste types with cementitious binders and/or design mixes that can overcome the incompatibilities. The latter goals require a thorough knowledge of the matrix and its interactions with many kinds of wastes. The present work will begin to build that knowledge base.

METHODS

The present report will describe the first of three phases of the work carried out to date. Phase 1 may be described as the fundamental research aspect of the work and began as an effort to understand solidification mechanisms using cement and several water-soluble organics. Phase 2 of the work is an extension of Phase 1 and involves cooperation with the Waterways Experiment Station of the U.S. Army Corps of Engineers (WES) in a project to characterize interferences by various inorganic and organic materials in solidification of metal sludges using cement and fly ash fixing agents. Phase 3 of the work involves use of x-ray diffraction (XRD) and scanning electron microscopy (SEM) to characterize vendor-produced samples of wastes solidified by processes which are usually proprietary. Phase 3 is a part of the USEPA/Environment Canada joint project to evaluate test methods for solidified products. Phases 2 and 3 are not completed because of delays in providing materials to carry out the LSU portion of the projects. Those two phases will be described in detail in a future report.

Since all three phases of the work use some of the same methods for characterization of solidified materials, the present report will begin with a detailed description of sample preparation and characterization methods. The methods are adaptations of procedures used in the characterization of cements (or other inorganic) matrices, as well as techniques common for solidified waste form characterization. The methods will be described in detail in individual sections below, but by way of introduction, the methods and the information they are expected to afford are summarized here:

Extraction with solvents of varying polarity: The samples containing various concentrations of organics are being ground to a standard size and extracted with three solvents, dichloromethane (DCM), dimethyl sulfoxide (DMSO) and deionized water. The amount of organic compound recovered in the extractions is determined as a function of solvent polarity and time of cure for the sample. The data are used to reach qualitative conclusions concerning the environment of the organic compound in the cement structure, and trends in extractability are compared with qualitative differences in sample morphological composition observed by microscopy.

Microscopy (Optical and SEM) and energy-dispersive x-ray analysis (EDXA): Optical and SEM observations of surfaces of solidified samples have been carried out in order to characterize changes occurring as a function of addition of wastes to cement. A huge number of micrographs has been published for cements alone, and with various additives, so that a large amount of data is available for comparisons. EDX analysis can provide an elemental profile of a solid surface, with certain limitations to be described below. These methods in combination with those described below can allow determination of whether the waste has influenced the formation of the mineral phases characteristic of the matrix.

Transmission electron microscopy (TEM) and selected area diffraction (SAD): The transmission electron microscope has been used to study ceramic materials and minerals for the past 30 years and several studies of cement have been reported. However, TEM has not been applied to studies of solidified hazardous chemical wastes. The main advantage of TEM is the high spatial resolution, which can exceed 0.2 nm. In addition, the SAD pattern can provide information about crystal structure and the orientation of crystalline phases. Both of these instrumental characteristics are important for waste research.

X-ray powder diffraction: Powder diffraction analysis allows the crystalline mineral constituents of the matrix to be identified by their characteristic set of diffraction lines. Many XRD studies of cements have been carried out. While there are limitations associated with the complex nature of the solid matrix formed, some mineral constituents are easily identifiable. The presence or absence of specific mineral phases can be a function of admixtures in the cement formulation, and that will presumably be the case also when wastes are the admixtures.

Physical testing: Selected physical characteristics of the solidified samples have been studied in order to define strength and practical workability of waste/cement mixes. Specifically, compressive strengths and setting times (initial and final) of cements containing organics were studied in this report. The compressive strength test reflects the amount of applied loading the solidified wastes can withstand before failure in a landfill. The setting time tests indicate the time needed for the solidified wastes to become workable. In addition, these tests were conducted because they have long been used by the cement industry as standard indicators of mechanical performance.

Experimental details of the methods used follow below.

Sample preparation

In the phase 1 work, the following procedures have been utilized. At the outset of the project we anticipated using organic and inorganic model wastes of a number of different types and in a wide range of concentrations. The result of this is that the "solidified" samples vary greatly in character from solid masses much like set cement, to non-solidified "soups", to solid masses with free-standing liquid.

Several ASTM and AASHTO standard methods requiring standard sample preparation techniques were reviewed for possible adoption. However, none of the standard methods of specimen preparation is strictly applicable to the conditions and requirements associated with the present research. In all the standard methods the wet consistency of the samples varies within reasonably narrow limits, and all of the cured products are hardened solids, conditions which are not always met by our samples. A further complication due to the heterogeneous nature of some of the samples in our work is that reliable partitioning of large solidified samples would not be possible. Hence each sample needs to be prepared separately and must be capable of being transferred quantitatively at each stage from mixing to curing to analysis. An additional concern in our work has been to limit any volatilization of an organic admixture during the curing period.

The experimental restrictions noted above have led us to chose to prepare and cure samples in the same container, using sealable glass scintillation vials. Special temperature control is not being applied, and room temperature is in the range 23° ± 2°C. Samples are being stored in the dark to avoid any possibility of photochemical reactions. Mixing of the samples is being done by low speed hand stirring for one minute after the mixed liquids are added to the unhydrated cement. Reliable replication in sample preparation is being judged by extraction behavior, to be described below.

The cement being used is obtained from River Cement Co., St. Louis, MO. Enough Type I Portland cement from a single batch has been obtained to use for the entire project. The analysis of the cement, expressed in terms of elemental oxides, has been provided by River Cement Co., and is shown in Table 1. The cement is being stored in plastic bags within air-tight plastic tubs. The chemicals being used are reagent grade materials which are not further purified, with the exception of p-aminomethylphenol, which was prepared and purified as described below. The solvents are spectrograde materials used without further purification.

Preparation of p-aminomethylphenol (pAMP)

The compound was synthesized using essentially the same procedure reported in the patent literature[3]. A mixture of p-hydroxybenzaldehyde (610 g, 5.0 mol), 28.8% ammonium hydroxide (1475 g, 25 mol), and 50% Raney nickel suspension in water (100 g) was placed in a 5 gallon autoclave, and 3 L of water was added as solvent. The air in the vessel was displaced with hydrogen at atmospheric pressure. The vessel was closed, and the reductive amination was carried out with H2 at a pressure of 70 - 75 psi and room temperature. The product was insoluble in the reaction mixture and precipitated out as the reaction proceeded. At the end of the reaction the white solid was filtered and the Raney nickel present in the crude product was separated by dissolving the product in hot methanol. The methanol was removed on a rotary evaporator to give a colorless solid (480 g, 78% yield). The compound was recrystallized from a mixture of chloroform and

Table 1. Percent Composition of Portland Cement Used in the Present Study

SiO_2	20.6%
Al_2O_3	5.2%
Fe_2O_3	2.4%
CaO	64.9%
MgO	3.3%
K_2O	0.6%
SO_3	2.9%

methanol to give colorless crystals (361 g, 59%), m.p. 108-110 °C (lit.[4] m.p. 109 °C).

Extractions and Analyses

Extraction procedure

The steps in sample preparation, extraction and analysis are listed below.

1. The required amount of organic compound (0.2 g, 0.4 g, 1.0 g or 2.0 g) is weighed out in a screw-cap vial, and 10.0 g of Portland cement is added, followed by 4.0 mL of deionized water. The mixture is stirred for 1 min. using a glass stirring rod.
2. The vial is allowed to stand in the dark at 23° ± 2°C for the prescribed amount of time (12 h, 24 h, 7 days, 28 days, 90 days or 1 year). The vial is broken and, if the mixture has hardened, the contents are ground by hand with a pestle in a mortar so that the mixture (with the exception of glass chips) will pass through a 100 mesh screen.
3. The contents, including glass pieces, are transferred to an Erlenmeyer flask, and 120 mL of solvent is added. The resulting mixture is shaken for 30 min. on a wrist-action shaker table, then filtered under suction through Whatman No. 41 filter paper.
4. The filtrate is analyzed for organic content by gas chromatography.

Because of the large number of samples to be prepared in the work and because of their extreme heterogeneity, we have been concerned with reproducibility from the beginning. The reproducibility of the extraction data serves as the principal criterion for reliability of the sample preparation technique. With occasional exceptions we can reproduce the amount of organic compound recovered from solidified samples prepared by our standard procedure and cured for the same length of time so that the standard deviation is <10% of the average of the values in three to six replicates. Usually it is <5%. The largest number of replicates we have done for any particular sample is 9, and that data is typical. The actual data for grams of ethylene glycol (EG) recovered from extractions of 9 separate preparations of 1:10 (by weight) EG:cement samples aged for 28 days is: 0.822 g, 0.796 g, 0.794 g, 0.779 g, 0.782 g, 0.764 g, 0.780 g, 0.762 g, 0.772 g. Each of the preceding numbers represents the analysis of a separate vial and is the average of three gc injections. These results give us confidence that the trends we are seeing are real. All of the preparations and extractions reported herein have been carried out at least in triplicate.

We have considered adding spikes to the ground cement samples to test the accuracy of the extraction procedure, but have not done so because of several complications. A significant component of hydrated cement pastes is unhydrated cement grains. When cement pastes are ground, release of the unhydrated grains allows hydration reactions to begin anew.[5] Consequently, to a significant degree, adding organic to the ground paste would be just like adding organic to the unhydrated cement powder in the first place.

Gas chromatographic analysis

Gas chromatographic analysis has been carried out using internal standards, as described in the "Standard Operating Procedures for the Analytical Support Laboratory and Associated Project Laboratories of the Hazardous Waste Research Center".[6] The three organic compounds being analyzed by gc in the present work are ethylene glycol (EG), p-bromophenol (pBP), and p-chlorophenol (pCP). The filtrate obtained after extraction is not concentrated prior to gc analysis. The concentration range observed in the filtrate is 5×10^{-4} M (for EG being extracted into DCM) to 0.60 M (for EG being extracted into DMSO or water). The internal standard is added in amounts required to give concentrations close to those of the organics being analyzed. In the cases of the phenols being extracted with water a pH adjustment is made to ensure that the phenol is in the protonated form. Extraction of the ground cement gives a very basic aqueous solution, and pH is adjusted to 7.0 using standard sulfuric acid solution prior to gc analysis. Extraction of solidified cement (without organic admixture), using DCM, DMSO or water as the extracting solvent, does not show any interfering components at a concentration close to 10^{-4} M.

The analytical work has been carried out on a Hewlett-Packard Model 5790 gas chromatograph equipped with a model 3390A reporting integrator. A flame ionization detector was used in all the work. The column used in all the work was a 6 ft. x 1/4 in. x 2 mm. 80/100 mesh Tenax glass column. The following internal standards were used: 1,3-propanediol for EG/DCM, EG/water, pBP/water, and pCP/water; p-cresol for pBP/DCM; p-t-butylphenol for pBP/DMSO; and butanol for EG/DMSO. The temperature programming conditions are given in Table 2. The data are expressed in grams of organic waste recovered or % recovery by weight.

UV analysis of pAMP

Because of the presence of both an acidic and a basic functional group in pAMP, and hence the possibility of existence as a zwitterion, analysis which depends on volatilization, as gc does, presents serious problems. Thus, the amount of pAMP recovered from the samples was analyzed by ultraviolet spectroscopy, since the presence of a chromophore in the molecule makes the quantitative determination by this method convenient. pAMP has two absorption maxima, at 240 and 290 nm in water and at 280 and 350 nm in DMSO. Since the shorter wavelength peaks are the more intense ones ($\pi \rightarrow \pi^*$), quantitation is done at 240 and 280 nm in water and DMSO, respectively.

Table 2. Gas Chromatograph Conditions

	EG/DCM	EG/DMSO	EG/H_2O	pBP/CM*	pBP/H_2O	pCP.H_2O
Temp. 1, ^oC	130	135	170	240	220	230
Time 1, min.	2.3	3.0	3.0	2.0	1.0	1.0
Rate, ^oC/min.	9.0	9.1	9.0	6.0	19.0	20.0
Temp. 2, ^oC	160	220	191	268	275	285
Time 2, min.	4.8	0	1.5	0	1.9	0.8
Inj. temp., ^oC	250	250	250	295	280	290
Det. temp., ^oC	250	250	250	280	275	285

*Also pBP/DMSO.

Measurements are carried out on a HP8451A diode array UV spectrometer. Control samples extracted with water and DMSO are used as reference for each calibration at different curing times. This eliminates any interference due to cement. Calibration standards are prepared from a stock solution containing 0.0231 g of pAMP in 25.0 mL of deionized water. The standards yielding concentrations ranging from 5 to 30 mg/L are made up to a total volume of 10 mL using the 12 hour water extract from the control sample.

A calibration curve is obtained by plotting concentration versus absorbance. The linearity is checked by the regression equation:

$$y = mx + c$$

where y = concentration in g/L, m = the slope of the line, x = the observed absorbance of the sample, and c = the intercept. The calibration curve shows a regression coefficient of 0.9990 with m = 12.53 and c = -0.9957. Using the equation just defined, the concentration of pAMP in all 12 hour samples is determined from the observed absorbance.

The same procedure is used for setting up a calibration curve for 24 hour water samples, with the regression line showing the following characteristics: regression coefficient = 0.9965, m = 12.30, c = 0.4876. A single calibration curve was used for 7 day and 28 day water samples, and that curve showed: regression coefficient = 0.9993, m = 12.34 and c = 0.4371. A single calibration curve was used for all DMSO samples, and it showed the following characteristics: regression coefficient = 0.9999, m = 61.28, c = 0.1907.

EP Tox extraction procedure

In some cases, in addition to the standard extraction procedure described above, the leaching test known as the USEPA Toxicity Characteristic Extraction Procedure (Method 1310)[7] was carried out. The structural integrity portion of the test was omitted. That segment of the procedure allows the leaching of a monolithic sample if it remains intact after 15 drops of a small hammer. However, the samples in this study were ground with a mortar and pestle until the material passed through a 9.5 mm (0.375 in.) standard sieve. We believed this procedure would result in a "worst case" scenario of maximizing surface area available for leaching. A 100 g sample was extracted in 1600 mL of deionized water containing the procedure limit of 400 mL of 0.5N acetic acid on a shaker table for 24 hours. After extraction, the samples were filtered through 0.45 µm filters using a vacuum filtration apparatus. The filtrate was then analyzed for the organic content by gas chromatography as described above.

Stability of pCP in a cement paste

p-Chlorophenol (pCP) has been used in our studies as a model compound for phenolic wastes in part because the x-ray emissions from chlorine atoms are readily detected in energy dispersive x-ray analysis (EDX), as described in a later section of this report. Given the low reactivity of aromatic C-Cl bonds, we have assumed that when Cl atoms were being detected in EDX analysis, the organic waste was being detected. The present work demonstrates that that assumption is correct. If the Cl atoms of pCP do not stay attached to the phenolic ring, then they will be released in the cement matrix as chloride ions. Consequently, we have analyzed for chloride ion in the water extract from cement samples with and without pCP in order to determine whether the addition of pCP increases the chloride ion concentration in the cement paste.

Samples were prepared as described above, cured for 28 days, ground to pass a 100 mesh screen and extracted with 120 mL of deionized water. The two samples in the present case were composed of 10 g of cement with 4.0 mL of water and 10 g of cement with 1.0 g of pCP and 4.0 mL of water. Chloride analysis of the water extracts was performed using EPA Method 325.3[8], which involves titration of an acidified aqueous solution with a standard mercuric nitrate solution using as indicator a mixture of diphenylcarbazone and bromphenol blue. Formation of a blue-violet complex of mercuric ions with diphenylcarbazone indicates that chloride ions are no longer available to consume mercuric ions.

The weight of chloride ion extracted from the two samples is indicated below:

	mg of Cl^-
control cement	0.30 ± 0.08
cement + 10% pCP	0.18 ± 0.04

The figures represent the weight of chloride in the 120 mL extracts from the samples. The uncertainty reported is ± one standard deviation in three titrations of the aqueous extract. There is very little chloride ion present in either sample. Clearly, the addition of rather large amounts of pCP does not increase the amount of chloride in the sample after 28 days of curing. Hence, it is safe to assume that chlorine which is attached to the aromatic ring of pCP when added to the cementitious mixture, stays attached to the organic moiety during the hydration process, and when we detect Cl in the cement paste, we are detecting the presence of the organic waste.

Microscopy (Optical and SEM) and energy-dispersive x-ray analysis (EDXA)

An EDAX International Model ECON-149-10 energy dispersive x-ray analyzer unit equipped with an EDAX 9100 computer mounted on an ISI-60A scanning electron microscope was utilized in the study. The SEM was operated at 15 keV accelerating voltage with a 150 μA filament current at a vacuum chamber pressure of $< 5 \times 10^{-5}$ torr. The low accelerating potential minized beam penetration yet allowed sufficient electron emission for good image contrast. Specimens were analyzed using an x-ray take-off angle of 64°. Atomic number, absorption and secondary fluorescence (ZAF) corrections for the semi-quantitative analyses were calculated by the FRAME C program installed on the EDAX 9100 computer. The background for this procedure was defined manually by a fitting mode of this program which uses a Reed-Fiori fit[9]. Spectra were collected for 200 live seconds of detector time, which corresponds to an 8,000 to 10,000 count Ca peak.

In the electron/specimen surface interaction within the SEM, x-rays are produced along with the secondary electrons used in creating the SEM image. The energies of these x-rays are characteristic of the element responsible for their emission. Collection, separation and enumeration of the characteristic x-ray energies is the basis of EDX. The intensity of these characteristic x-rays changes with the tilt angle of the specimen surface because of differences in backscattering and absorption. This fact, along with the danger of x-ray emission from projections on the specimen surface which may intercept backscattered electrons or x-rays, explains the importance of a flat, smooth specimen surface for reliable quantitative analysis.

Fracture surface sample preparation

In the fractured surface SEM observations discussed herein, specimen preparation began by immersing the sample in liquid nitrogen for approximately one hour. The purpose of freezing was to minimize plastic deformation during breakage. The frozen sample was wrapped in a clean cloth and struck sharply with a heavy object. A relatively flat specimen was selected from the center of the sample to avoid the possible influence of the glass vial sides on solidification. This specimen was attached to an aluminum stud with silver paint and placed in a vacuum or a dessicator to dry. A 200 A carbon coating was applied to the surface using a Denton DV-502 vacuum evaporator to prevent charge buildup. Specimens were stored in a dessicator, at ambient temperatures, until examined.

Polished surface specimens

Preparation of thin sections for optical microscopy and EPMA followed typical petrographic procedures. The sample was broken in half laterally, and the inside surface was polished on 400, then 600 mesh abrasive paper until smooth. This surface was then glued to a glass slide with Hillquist thin section epoxy and cured for 24 hours. Next, the specimen was sliced close to the slide with a diamond saw and polished successively with 400, 600 and 1000 mesh abrasive powders. Final polishing was performed using 6 μm alumina powder. It is important to note that at no time was water used during this procedure. Lubrication, cooling and washing was performed with isopropyl alcohol. The thickness of the thin sections was approximately 30 to 40 μm. For EPMA analysis a 200 A carbon coating was evaporated onto the specimen surface using a Denton DV-502 vacuum evaporator.

For EDXA analysis in the SEM, specimens were mounted on a 1 in. (25.4 mm) by 1.3 mm by 10^{-2} mm cylinder of plastic Kold Mount. Before polishing, the specimens were impregnated with a hard polymer to insure rigidity. The impregnation process consisted of the following steps. A small specimen (ca. 5 mm long and 2 mm thick) was taken from the center of the sample cylinder, degassed in a vacuum chamber for about 1 hour, then immersed in the polymer and placed in a vacuum oven at ambient temperature for 24 hours. The specimen was then heated under vacuum to 60 ± 5 °C for another 24 hours, then mounted and polished as previously described. A 20 nm gold-palladium coating was applied to the specimen to prevent charging effects in the SEM.

Transmission electron microscopy (TEM) and selected area diffraction (SAD)

The specimen suitable for TEM examination must be very thin (100 nm at 100 keV) to allow penetration of the electron beam. The thin specimen is usually obtained by replica techniques, by ion thinning, or by ultramicrotomy. The replica technique, used in the present study, reproduces the topography of the specimen surface. Cements are composed of several particle-like phases, and their surfaces are porous. During replication an occasional mineral particle is extracted onto the acetate film. Therefore, in addition to the morphological structure being preserved in the carbon film, extracted particles are sometimes observed. Some thin crystalline particles were suitable for obtaining electron diffraction patterns.

All hydrated cement samples were ground with silicon carbide papers using grit sizes from 180 to 600. Specimens were polished with diamond paste on a rotating wheel using propanol as a lubricant. Rinsing was also done with propanol rather than water in order to prevent further hydration. The cleaned specimen was replicated by a cellulose acetate tape wetted by acetone. After the plastic tape had dried, it was stripped off the specimen and then coated with carbon in a vacuum evaporator. The carbon film was then cut into small pieces (ca. 9 mm^2) and washed with acetone. After the plastic dissolved, the carbon film was caught on an electron microscope grid for TEM study. Specimens were examined with a JEOL 100-CX TEM operated at 100 keV.

X-ray powder diffraction

A crystalline phase will diffract a monochromatic beam of x-rays when Bragg's Law (equation 1) is satisfied for a particular

$$n \lambda = 2 d \sin \theta \qquad (1)$$

crystal. In equation (1), n is the multiple of the wavelength, λ is the wavelength, d is the spacing between two successive atomic planes of the phase of interest, and θ is the diffraction angle.

Copper, iron or molybdenum x-radiation are commonly used. Cu $K\alpha$ has higher wavelength than Mo $K\alpha$, and copper radiation is thus more suitable for phases with higher d-spacings. Any crystalline sample can be studied by the x-ray diffraction method. Finely crushed powder of the sample is gently packed into a rectangular recess in a metal plate. In order to obtain accurate information about the sample it is necessary that many crystallites in random orientations be present. This will ensure that reflections from all the different atomic planes in the phases present in the sample are obtained.

In x-ray diffractometry, while the sample is irradiated with suitably collimated, monochromatic x-ray radiation, it is slowly rotated at a fixed speed, thereby changing the angle θ in Bragg's equation. The detector is rotated at the same time at twice the speed to maintain the proper geometric relationship. When Bragg's law is satisfied for a particular phase, a strong signal is produced and recorded by a strip chart recorder which is moved at a proportional speed. The run of one sample will thus produce a series of peaks superimposed on a background due to random scattering of x-rays where the horizontal scale is the 2θ angle and the vertical scale is proportional to the intensity (counts per second, cps). The 2θ values at which the peaks occur can be read off the chart, and the d-spacings of the phases which produced these peaks can be calculated from Bragg's equation with the 2θ values and the wavelength λ of the x-ray radiation used. In general, a sample will produce a set of d-spacings and their relative intensities.

A compilation of d-spacings of well-characterized organic and inorganic substances has been produced by the Joint Committee on Powder Diffraction Search (last updated in 1984). The d-spacings found from the unknown sample can be compared with those of the known compounds and the phases present in the unknown thus identified. The process of identifying the unknown phases in a sample is straightforward when only a few well-characterized phases are present. For Portland cement, where the reaction products are poorly crystalline and may exist as solid solutions, identification of different phases is more difficult.

The XRD runs were made with a Rigaku DMAX automated x-ray diffractometer. The intensities were digitally recorded. Mo Kα or Cu Kα radiations were used for the runs. For Cu Kα radiation, the voltage was 40 kV and the current was 30 milliamp. The slit widths after the sample were 4 and 1 mm, respectively. The samples were scanned from 3 to 70° 2θ, and the scan rate was 0.02° 2θ per second. For Mo Kα runs, the 2θ values ranged from 3 to 36°. The step width was 0.01° 2θ and count time at each step was 1 s. The other parameters were similar.

Aluminum powder was added as an internal standard in each sample. Al has several widely separated, sharp, well defined peaks. The peaks produced from the phases present in the sample can be measured from the Al peaks and thus any calibration problems with the diffractometer can be circumvented.

Physical testing

The compressive strength test was performed according to the

Standard Test Method for Compressive Strength of Hydraulic Cement Mortars Using 2 inch or 50 cm Cube Specimens (ASTM designation C109-80). The cement mix contained 650 g of cement, 260 mL of deionized water and either 26, 65 or 130 g of one of the organic compounds. Standard 2 inch cube molds were used to cast specimens. After removal from the molds, cubes were stored in air-tight containers at room temperature. Curing times of 12 hours, 1 day, 7 days and 28 days were used. Three specimens were tested for each mix on a Riley electrically driven, hydraulic type compression testing machine.

The setting times were determined according to the Standard Method of Test for Time of Setting of Hydraulic Cement by Vicat Needle (ASTM designation C191-74). The initial setting time is the time at which a standard needle penetrates 25 mm into the sample. Final setting time is the time at which a second needle penetrates its point into the cement but the ring around the point does not indent the sample. Although the test is regularly performed at the water content that gives normal consistency to the cement (i.e., when a 300 g rod having a diameter of 1 cm settles to a point 10 ± 1 mm below the surface of a representative sample, within 30 s after being released), in this test the 0.4 water/cement ratio was used in each case.

RESULTS AND DISCUSSION, PHASE 1

Phase 1 of the present study involves studies aimed at characterizing the interactions of organic compounds with cementitious stabilizing materials. Solidification/stabilization technology has been most commonly applied to inorganic waste streams, notably those containing toxic metal ions. However, there are many waste streams which contain large amounts of hazardous metal constituents, but which also contain substantial amounts of organics. Solidification/stabilization would be a reasonable choice as a disposal option; but considerable uncertainty is associated with the presence of the organics in the mixture. A limitation often cited with respect to commercial fixation processes is that they are incompatible with organics, but details of such incompatibility are generally not available.[2] A potential concern is that organics, even in small amounts, can alter the process sufficiently to substantially decrease the ability of the fixing agents to immobilize metal ions. Indeed, it is well known that organics can alter the setting characteristics of Portland cement, which is one of the principal constituents of many commercial fixing agents. It is not clear whether, and at what concentrations, organics interfere with the relatively complex setting reactions resulting in a significantly altered cement matrix. The question is of interest, not just with respect to solidification/-stabilization technology, but also with regard to fundamental understanding of cementing reactions. Clearly, also, if cementitious techniques are to be successful in immobilization of hazardous organics themselves, fundamental understanding of bonding and interfering mechanisms associated with the processes must be developed.

Keeping in mind the concerns expressed above, we have framed the following scientific questions to be addressed in the present work relating to organic/cement systems:

1. Is the process mainly one of physical entrapment, or do some chemical binding forces exist between organic and matrix? If the latter occurs, what classes of organics participate?
2. What chemical transformations do the organics undergo during solidification/stabilization?
3. Are the interactions concentration- and time-dependent?
4. How is the integrity of the cement matrix affected by the presence of the organic?

The bulk of the work to be reported here has involved studies of relatively polar organic molecules, although some preliminary work with nonpolar organics will also be reported. Because of their relatively high water solubility, polar organics are the ones most likely to be present in substantial concentrations in mixed aqueous waste streams which also contain metal ions, and thus are good candidates as solidification/stabilization interferences. Glycols and phenols are typical of such species and are also major articles of commerce and hence constituents of waste streams. The main body of the work with organics carried out to date in our laboratories has involved ethylene glycol (EG), p-chlorophenol (pCP) and p-bromophenol (pBP). The reason for choosing halogenated phenols, apart from the fact that they are typical of real wastes, is that the presence of the heavy atoms enables elemental analysis by energy dispersive x-ray analysis in order to locate the organic within the complex hydrated cement matrix. This aspect of the work will be reported in a later section.

Polyhydroxy compounds are in fact among the classes of organics which alter the setting characteristics of Portland cement. When, for whatever reason, mixed concrete cannot be promptly laid, it is a common trick of the trade to throw in a bag of sugar as a set-retarder. The effects of relatively small amounts (up to 0.5%) of triethanolamine (TEA) on the setting characteristics of Portland cement have been studied, mainly using differential thermal analysis, thermogravimetric analysis and conduction calorimetry[10]. At amounts from 0.17 to 0.5%, TEA greatly accelerates the initial set, but retards the final set and produces a weaker cement structure. The results have been interpreted in terms of "a complex formed between TEA and the hydrating components of portland cement".

The polyhydroxy organic, ethylene glycol (EG), was chosen for the present study for several reasons. There is evidence in the literature that EG has profound effects on already set cement and the mineral constituents thereof[11,12]. When hydrated cement or tricalcium silicate (C_3S) is treated with EG, etching occurs, but it is unclear whether mainly calcium silicate hydrate gel (CSH) or calcium hydroxide (CH) is dissolved[12].

A further consideration is that EG is completely miscible with water, and hence cement pastes can be prepared with any concentration of EG in water, and in all cases a homogeneous liquid phase is being mixed with the unhydrated cement. The mixing problems are also minimized with the phenols, which are acidic enough (pKa = 9.6 for pBP) to be converted essentially completely to water-soluble phenoxide salts under the very basic conditions of hydrating cement pastes (pH > 11). When the very water-insoluble organic, 1-decanol, was solidified, as the weight ratio of organic to cement varied from 50:1 to 1:1, the product of solidification varied from a solid indistinguishable by the naked eye from hardened cement to a two-phase system with hardened material and supernatent liquid (shown by gc analysis to be pure 1-decanol). With the EG samples, there was great variation in the physical appearance of the mixes as functions of both concentration and time of cure, as shown in Table 3.

EXTRACTION STUDIES

The extractions were conceived as having a two-fold purpose: (1) to obtain qualitative data about the nature of the binding of the organic to the cement from the conditions of extraction required to recover the organic and (2) to get back as much of the organic and its reaction products as possible in order to characterize any reaction chemistry occurring during solidification. The second aim was unnecessary for the particular organics studied here. No evidence of any organic reaction products was seen in any of the extractions. That is not surprising, since the organics chosen for the first phase of the study could be expected to undergo only ionization reactions under the basic aqueous conditions characteristic of setting cement. Future work with other organics may be concerned with identification of reaction products.

The three solvents being used in the extractions are dichloromethane (DCM), dimethylsulfoxide (DMSO) and water. They differ substantially in polarity, as measured by either dielectric constant (8.9, 47 and 80, respectively) or polarity index[13] (3.1, 7.2 and 10.2, respectively). Changing solvent polarity would be expected to have a number of possible effects on the extraction behavior. Intermolecular interactions between EG and the solvents, particularly dipole-dipole and hydrogen bonding, will increase in the order DCM < DMSO < H2O. The extent of extraction will depend upon the magnitude of these forces in comparison to those between the organic and the cement matrix. The solvent interactions with the cement matrix itself will also vary. The ability of water to dissolve $Ca(OH)_2$, and perhaps other constituents as well, out of the cement paste could mean that water penetration into the material would be greater than that of the other solvents, thus having the effect of freeing more of any organic which was simply physically trapped in areas of the matrix inaccessible to a less aggressive solvent. We are not convinced that the latter argument is valid under our conditions using ground samples. When 1-decanol is solidified with cement and extracted with DCM, >85% of the decanol is recovered. Clearly our grinding and extracting pro-

TABLE 3.

Appearance of Ethylene Glycol/Cement Samples

	Time of Cure				
Ratio*	12 h	24 h	7 d	28 d	90 d
1:50	Soft and Wet	Soft and Wet	Hard and Dry	Hard and Dry	Hard and Dry
1:25	Soft and Wet	Soft and Wet	Hard and Dry	Hard and Dry	Hard and Dry
1:10	Soft and Wet	Soft and Wet	Hard* and Dry	Hard* and Dry	Hard* and Dry
1:5	Very Soft, Wet	Very Soft, Wet	Soft* and Wet	Slightly* Hard, Wet	Hard* and Dry
1:2	Very Soft, Wet	Very Soft, Wet	Soft and Wet	Soft and Wet	Soft and Wet
1:1	All samples had standing liquid on top, a middle layer which was light colored with loose cement, and a bottom layer which was darker in color and was a soft cement block.				

*These samples were pink in color when prepared from one batch of Type I Portland cement supplied by River City Cement Co. Subsequent River City cement, including that used for all the subsequent work, did not give pink samples.

cedure does free most of the physically entrapped organic, and it is being recovered by a solvent which would not be expected to dissolve any of the cement matrix.

Extractions of 1-decanol

Initial extraction work was performed on samples prepared using 1-decanol, a water-insoluble hydrocarbon-like organic. We wanted to find out from this work whether an organic which would be expected to have little chemical interaction with a cement matrix (but does have the possibility of hydrogen bonding interactions by virtue of the presence of an OH group) could actually be essentially completely recovered by our extraction procedure using a solvent expected to interact strongly with the organic, but not with the matrix; namely, DCM. If this is the case, then our grinding procedure is capable of freeing the majority of organic inclusions which are simply physically entrapped. Table 4 contains extraction data on a sample of one part (by weight) decanol to ten parts cement and four parts water. The sample is a hardened block which requires grinding before extraction. The results shown are for extraction with DCM. These results indicate that the percent recovery is reasonably reproducible from sample to sample and confirm our expectation that there is little binding of decanol to cement, since percent recovery is large. Repeated extraction of the same sample results in overall recovery of 97% of the decanol (Table 5). The remaining 3% may be physically trapped in pores in the cement matrix which remain inaccessible to solvent after our grinding procedure. Table 6 shows the effect of a variable amount of grinding on the percent recovery of decanol in a single extraction with DCM. As expected, the finer the particles before extraction, the greater the recovery. Again, a reasonable interpretation of the finding is that physical entrapment is the major mechanism operating for binding of decanol.

Extractions of ethylene glycol (EG)

The first extensive set of extractions of samples containing varying ratios of organic to cement and at varying times of cure were performed on samples with EG, a water-soluble organic which will be in intimate contact with the cement during the setting reactions. EG is very soluble in all of the solvents used in the extractions, so that solubility alone cannot be assumed to determine the amount of EG recovered by extraction. The percent recoveries reported in Table 7 for extraction from 1 month-old samples prepared with various weight ratios of EG to cement reflect the expectation that chemical interactions of EG with water will be greater than those with DMSO or DCM. Since DCM and DMSO extract relatively small amounts of EG (compared to water), and since our procedure appears to free most physically entrapped organic, the reasonable conclusion to draw is that there is some chemical interaction between EG and the cement matrix that is stronger than the EG-DCM and EG-DMSO intermolecular interactions.

The loading of EG in the cement samples might be expected to influence extractability very substantially, since bound EG could be in quite different environments, and the cement matrix might be quite different at different EG concentrations (see microstructural characterization described in a subsequent section). Surprisingly, as is typical of solvent extractions which can be characterized by a single extraction coefficient, the percent recovery of EG is approximately the same with varying content of organic in the

Table 4. Recovery of 1-Decanol from Cement as a Function of Volume of Dichloromethane (DCM) used for Extraction

Volume of DCM	Percent Recovery of 1-Decanol			
	Run 1	Run 2	Run 3	Average
60 ml	86.8	85.8		86.3
120 ml	89.0	88.8	89.0	88.9
180 ml	89.2	91.1	92.5	90.9

Table 5. Multiple Extractions of Decanol/Cement* with CH_2Cl_2

Extraction	Percent Recovery			
	Run 1	Run 2	Run 3	Average
1	89.8	89.6	89.9	89.8
2	6.8	6.7	6.8	6.8
3	0	0	0	0

Total Recovery = 96.6 Percent

*1.0 g decanol + 10.0 g cement + 4.0 ml H_2O

Table 6. Recovery of 1-Decanol from Cement as a Function of Particle Size*

Particle Size	Percent Recovery of 1-Decanol			
	Run 1	Run 2	Run 3	Average
No Screening (>60 mesh)	77.9	80.5	80.1	79.5
60 mesh	83.3	84.6	88.0	85.3
100 mesh	86.8	85.8		86.3

*each run was the result of an extraction with 60 mL of dichloromethane on a sample made from 1.0 g decanol, 10.0 g Portland cement and 4.0 mL water. The sample was extracted 48 hours after preparation.

Table 7. Percent Recovery of EG in Extractions with Various Solvents at Differing EG/Cement Weight Ration

	% Recovery			
Wt. Ratio	DCM	DMSO	dil* base	dil** acid
0.02	3.7	12	79	95
0.04	3.4	11	79	89
0.10	6.5	15	89	76
0.20	7.0	43	83	79
0.50	5.1	54	79	79
1.0	4.8	-	84	81

*The water solution was initially 0.05M in Na_2CO_3 and 0.05M in $NaHCO_3$, with an initial pH of 9.9. The pH after extraction was 13.
**The water solution was initially 0.05M in acetic acid and 0.1M in sodium acetate, with an initial pH of 5.0. The pH after extraction was 12.

samples, except in the case of DMSO extractions. In the DMSO case there is a major break in behavior between weight ratios of 0.1 and 0.2. These results suggest that at high loadings a larger proportion of the EG is very loosely bound. The difference between those environments shows up with DMSO extraction but not with water or DCM extractions, because in the former case the magnitudes of EG-solvent interactions and EG-cement interactions are more closely balanced.

The extent to which any EG may be irreversibly bound in the cement matrix has been investigated by repeated extractions of the same sample with water and DMSO (Table 8). In these experiments the solid residue after the initial extraction was treated with a second 120 mL of solvent, reshaken, refiltered and analyzed. The samples were ground only one time. All of the EG has not been recovered after 5 extractions with the most aggressive solvent, water. Evaporative losses are possible, but we are using a very non-volatile organic, and deliberately allowing the solids to stand open to the air for an hour or more prior to extraction did not affect the results. We conclude that there are sites where EG is bound more tightly than by surface hydrogen bonding and/or that there are sites in the cement matrix that are very poorly accessible to water.

The age of the sample affects extraction behavior (Tables 9 - 11). Again, the DMSO extractions are most indicative of a changing EG environment, with steadily decreasing percent recoveries up to 90 days of cure. At high loadings the decrease in % recovery does not really begin until after 7 days of cure. As is indicated in the physical testing to be described below, EG very substantially retards the set of cement, and the matrix is thus slower to develop with increasing amounts of EG present.

The extraction results suggest that when EG is solidified with cement, the EG appears to occupy at least three different kinds of environments. At high EG concentrations there is a significant amount of very loosely bound EG, which can be extracted readily by either DMSO or water, but not by DCM. The second environment contains more tightly bound EG, probably bound to surfaces by hydrogen bonding, and such EG can be readily extracted by water but not by DMSO. The EG still remaining after repeated extractions with water or DMSO can be considered to occupy a third, even more tightly bound, environment. Conceivably this environment could be one in which EG replaces water of crystallization in some of the crystalline structures. However, as discussed below, alterations are obvious by XRD and TEM in the semi-crystalline CSH gel phase, and we suggest that the EG is located there. The Feldman-Sereda model[14] of hardened cement paste includes an environment for water between layers of CSH. EG could substitute for water in such an environment and be both chemically bound, probably mainly by hydrogen bonding, and also physically inaccessible to extracting solvents.

Ethylene glycol was also solidified in the presence of organosilicon "coupling agents". The coupling agents are materials used in the preparation of composite materials, i.e., plastics with

Table 8

Percent Recovery of Ethylene Glycol
in Extraction with DMSO

	Percent Recovery				
Ratio*	12 h	24 h	7 d	28 d	90 d
1:50	57	32	7.6	4.2	5.7
1:25	67	44	8.8	11	6.3
1:10	90	74	28	19	19
1:5	85	84	80	42	36
1:2	91	88	82	47	49
1:1	90	90	81	69	56

*Weight ratio of EG to cement. Ratio of water to cement is 0.4 in each case.

Table 9

Percent Recovery of Ethylene Glycol
in Extraction with DCM

	Percent Recovery				
Ratio*	12 h	24 h	7 d	28 d	90 d
1:50	4.8	5.0	4.5	3.7	2.2
1:25	4.6	5.0	5.8	3.4	2.1
1:10	6.1	5.1	5.7	6.5	3.3
1:5	6.2	6.0	5.9	7.1	5.3
1:2	4.6	4.2	4.6	5.1	4.1
1:1	4.1	3.7	3.7	4.8	2.7

*Weight ratio of EG to cement. Ratio of water to cement is 0.4 in each case.

Table 10

Percent Recovery of Ethylene Glycol in Extraction with DMSO

	Percent Recovery				
Ratio*	12 h	24 h	7 d	28 d	90 d
1:50	57	32	7.6	4.2	5.7
1:25	67	44	8.8	11	6.3
1:10	90	74	28	19	19
1:5	85	84	80	42	36
1:2	91	88	82	47	49
1:1	90	90	81	69	56

*Weight ratio of EG to cement. Ratio of water to cement is 0.4 in each case.

Table 11

Percent Recovery of Ethylene Glycol in Extraction with Water

	Percent Recovery				
Ratio*	12 h	24 h	7 d	28 d	90 d
1:50	91	76	83	81	71
1:25	95	90	89	88	76
1:10	91	88	80	78	75
1:5	88	86	83	81	78
1:2	87	84	82	75	78
1:1	81	82	80	78	70

*Weight ratio of EG to cement. Ratio of water to cement is 0.4 in each case.

inorganic constituents. The coupling agents serve as bridges between the organic and inorganic components, in most cases allowing covalent bonding between the two components of the composite[15]. Only a small amount of coupling agent is required in order to greatly influence the physical properties of the composite blend. We envisioned a comparable effect in the present work, in which the inorganic cement matrix might be rendered more organophilic by reaction of surface OH groups with the alkoxysilane coupling agents. The results in Table 12 indicate that that expectation was not realized. In no case was the percent recovery in a water extraction lowered by the presence of the organosilane.

Extractions of phenols

Phenols represent a very common disposal problem in their own right as well as being a common ingredient in waste streams which contain toxic inorganic metal ions as well. Since the metal ions are commonly treated by solidification/stabilization using cementitious agents, two basic kinds of knowledge become important in order to assess the possibilities that solidification/stabilization will be successful in mixed waste streams. 1) What are the effects of various concentrations of phenols on the solid matrix being formed? Is the matrix compromised with respect to its durability and ability to immobilize metal ions? 2) What happens to the phenol itself under the solidification conditions and what are the chances that the phenol can be immobilized?

Two classes of phenols are of real interest because of their commercial importance and the frequency with which they may be encountered in waste streams. Those two classes are: 1) phenolitself and alkylated phenols, which are disinfectant and antioxidant materials, and 2) chlorinated phenols, including in particular polychlorinated materials present in products for wood treatment, such as creosote. These are organic materials, but their chemistry is so different from that of nonpolar hydrocarbon oils and greases that the two classes of organics present entirely different problems in solidification/stabilization. The principal problem which one must deal with in handling phenols is their very substantial water solubility, particularly under the conditions normally used for solidification. Those conditions are quite basic and result in conversion of the phenol to its phenoxide anion, and the latter is very much more water soluble than the unionized phenol.

Because of their common occurrence, their toxicity and because of an appreciation of some of the problems which they will present in solidification/stabilization, there is work already in the literature. Cote, et al. have presented data from dynamic leaching tests of solids prepared from a synthetic waste containing As, Cd, Cr, Pb and phenol which had been solidified using four different solidifying agents; namely, lime/fly ash; cement/fly ash; cement/-bentonite and cement/soluble silicate[16]. In all cases phenol was very rapidly leached, with greater than 50% recovery after 6 months. By contrast, the metal ions showed 2% or less recovery after 11 months.

TABLE 12
Extraction of EG from EG/10 Containing Organosilanes

Curing Time - 7 Days

Organosilanes	Solubility & Setting	Grams of Silane in EG/10	Amount of EG Recovered in Grams		EG Percent Recovery	
			Water	DMSO	Water	DMSO
None	-		0.811 0.799 0.824 0.808 0.795 0.791	0.282 0.280 0.296 0.270 0.260 0.306	80	28
3-Chloropropyltrimethoxysilane	Insoluble in EG, H_2O Soluble in DMSO 1 gram in EG/10 solidifies quickly during mixing 0.1 gram in EG/10 is non-solidified	1.000 1.000 1.000	0.951 0.966 0.947	0.985 0.959 0.960	95	97
		0.100 0.100 0.100	0.847 0.849 0.822	0.453 0.431 0.405	84	43
[2-(3,4-Epoxycyclohexyl)ethyl]trimethoxysilane	Insoluble in EG, H_2O Soluble in DMSO 1 gram in EG/10 solidifies quickly during mixing 0.1 gram in EG/10 is non-solidified	1.000 1.000 1.000	0.994 0.992 0.988	0.970 0.998 0.991	99	99
		0.100 0.100 0.100	0.882 0.878 0.867	0.508 0.476 0.478	88	49
(γ-Glycidoxypropyl)trimethoxysilane	Insoluble in EG, H_2O Soluble in EG, DMSO 1 gram and 0.1 gram in EG/10 are non-solidified	1.000 1.000 1.000	0.837 0.819 0.830	0.600 0.627 0.620	83	62
		0.100 0.100 0.100	0.882 0.863 0.891	0.756 0.757 0.782	88	76
Sodium Methylsiliconate	Soluble in EG, H_2O and DMSO 1 gram in EG/10 doesn't solidify while mixing but solidifies immediately after closing the cap. 0.1 gram in EG/10 is non-solidified	1.000 1.000 1.000	0.873 0.859 0.865	0.266 0.276 -	87	27
		0.100 0.100 0.100	0.877 0.847 0.841	0.418 0.428 0.396	85	41

The work reported herein also clearly demonstrates the ready leachability of phenols from cementitious fixing agents by water. We have investigated p-bromophenol (pBP), p-chlorophenol (pCP) and p-aminomethylphenol (pAMP). With DCM and DMSO as extracting solvents, we observed very low percent recoveries and no apparently meaningful trends as a function of phenol loading. Water extraction data as a function of phenol/cement ratio and time of cure is presented in Tables 13 and 14 for pBP and pCP. All the numbers are large. They are somewhat larger with pCP than pBP. That may be significant in a way to be explained later. As should probably be expected, as cure progresses, the % recovery decreases, although there are some irregularities with pBP that we can't explain. Both sets of data show the initially surprising result that as concentration increases, the % recovery initially increases, but then decreases again. We propose that at lower phenol concentrations there is plenty of hydroxide available to convert all the phenol to phenoxide. The phenoxide salts, whether Br-containing or Cl-containing, are quite water soluble and readily extractable. At higher phenol concentrations, significant fractions of the phenol go into the matrix as unionized phenol, which is less water soluble and less readily extractable.

We have done some extraction work with a third substituted phenol, which we think bears out the reasonableness of our assumptions. We have prepared p-aminomethylphenol. Table 15 shows two parameters called π and E_s. The former is a measure of affinity

Table 15

Hydrophobicity and Size Parameters[17]

Substituent	π	E_s
H	0	0
F	0.14	-0.46
Cl	0.71	-0.97
Br	0.86	-1.16
OCH_3	-0.02	-0.55
SCH_3	0.61	-1.07
$SeCH_3$	0.74	-
CH3	0.56	-1.24
CH_2CH_3	1.02	-1.31
CH_2NH_2	-1.04	-1.25
CH_2OH	-1.03	-1.21

TABLE 13
Para-Bromophenol Extraction with Water

Ratio	Amount of pBP Recovered in Grams						pBP Percent Recovery					
	12 Hours	24 Hours	7 Days	28 Days	90 Days	364 Days	12 Hours	24 Hours	7 Days	28 Days	90 Days	364 Days
1:50	0.123 0.127 0.143* 0.129 0.131 0.125	0.096 0.102 0.102 0.099 0.089 0.095	0.142* 0.119 0.116 0.113 0.114 0.110	0.055 0.055 0.054 0.052 0.050 0.051	0.141* 0.103 0.105 0.093 0.090	0.077* 0.074 0.070 0.064 0.061 0.057*	64	49	57	26	49	34
1:25	0.270 0.274 0.267 0.271 0.261 0.261	0.214 0.218 0.212 0.219 0.218 0.212	0.250 0.240 0.249	0.171 0.171 0.166 0.170 0.168 0.165	0.273 0.257 0.265	0.062 0.061 0.056 0.059 0.055 0.057	67	54	62	42	66	15
1:10	0.431 0.436 0.435 0.434 0.445 0.442	0.428 0.463 0.451 0.420 0.466 0.429	0.552 0.562 0.563 0.526 0.560 0.525	0.487 0.473 0.483 0.481 0.496 0.510	0.563 0.566 0.577	0.083 0.089 0.087 0.097 0.090 0.092	44	44	55	49	57	9
1:5	1.009 1.077 1.031 0.988 1.050 1.027	0.921 0.882 0.923 0.969 0.780	0.404 0.405 0.413 0.434 0.413 0.402	0.437 0.457 0.428 0.431 0.423 0.421	0.453 0.447 0.439 0.424 0.401 0.413	-	52	45	21	22	22	-
1:2	2.169 2.154 2.304	1.967 2.039 2.067	1.286 1.233 1.293	1.093 1.036 0.983	0.529 0.476 0.489	-	44	40	25	21	10	-
1:1	3.296 2.984 2.862	2.501 2.728 2.661	2.362 2.445 2.338	2.610 2.737 2.764	1.604 1.731 1.796	-	30	26	24	27	17	-

*Outlying value not included in the averaged numbers

TABLE 14
p-Chlorophenol Extraction with Water

Ratio	Amount of pCP Recovered in Grams 12 Hours	24 Hours	7 Days	28 Days	90 Days	pCP Percent Recovery 12 Hours	24 Hours	7 Days	28 Days	90 Days
1:50	0.154	0.122	0.095	0.093	0.071	76	63	48	46	36
	0.152	0.126	0.097	0.096	0.076					
	0.156	0.126	0.099	0.094	0.072					
	0.149	0.124	0.100	0.087	0.075					
	0.150	0.126	0.091	0.090	0.070					
	0.151	0.126	0.097	0.087	0.074					
1:25	0.318	0.313	0.278	0.225	0.223	80	78	68	55	53
	0.312	0.316	0.276	0.225	0.209					
	0.327	0.309	0.273	0.228						
	0.322	0.314	0.269	0.223	0.202					
	0.332	0.306	0.273	0.213	0.219					
	0.319	0.317	0.270	0.216						
1:10	0.943	0.810	0.632	0.610	0.615	93	82	64	62	60
	0.939	0.821	0.645	0.605	0.612					
	0.944	0.800	0.645	0.616	0.601					
	0.906	0.832	0.654	0.633	0.601					
	0.936	0.828	0.631	0.608	0.572					
	0.917	0.816	0.631	0.630	0.533*					
1:5	1.928	1.894	0.922	0.876	0.897	97	95	45	43	45
	1.939	1.924	0.915	0.842	0.928					
	1.934	1.896	0.875	0.874	0.902					
	1.915	1.896	0.936	0.870	0.939					
	1.935	1.862	0.856	0.873	0.866					
	1.942	1.876	0.862	0.883						
1:2	3.378	3.331	2.713			67	67	56	49	48
	3.409	3.345	2.883	2.542	2.406					
	3.216	3.285	2.877	2.427	2.378					
	3.438	3.449	2.571*	2.397	2.475					
	3.410	3.299	2.794							
1:1	4.008	3.685	3.578	3.857	4.091	37	36	37	38	39
	3.588	3.772	3.535	3.757	3.910					
	3.457	3.502	4.062	3.652	3.681					

for water that is conferred by the substituent group, and the latter is the size. The three substituents, Cl, Br and CH_2NH_2 show a trend of increasing size, but the amine-containing group is much more hydrophilic, and thus water soluble. Table 16 shows the difference in extraction behavior which this difference in hydrophilic character results in. Now the numbers are larger and there is no maximum going down the table. Both the salt and the unionized phenol are so water soluble that they are easily extracted.

SEM AND ENERGY DISPERSIVE ELEMENTAL ANALYSIS

Ethylene glycol samples

EG contains only light elements, and the particular elements are common constituents of cement pastes without EG present. Consequently, elemental analysis of EG-containing samples was not attempted. Nevertheless, useful information may be obtained by observation of morphological characteristics. Calcium silicate hydrate (CSH) and calcium hydroxide (CH) together constitute over 75% of a typical cement paste and are distinguishable by their morphological characteristics. CSH "gel" constitutes one-half to two-thirds of the volume of hydrated pastes and consequently strongly influences their behavior. CH crystals consitute 20% to 25% of the paste volume. As the paste ages, CH becomes an increasingly prominent constituent of the microstructure and is characteristically observed as hexagonal plates. SEM micrographs reveal both CSH and CH in both plain and EG-containing cements.

Of considerable practical interest is the concentration of organic required to make significant changes in the cement matrix. It is reasonable to assume that if the matrix is considerably altered, the ability of the matrix to immobilize both metal ions and organics will be altered. SEM observations of the gross morphology of fracture surfaces of the solidified samples reveal few obvious differences between specimens of hydrated cement alone and hydrated cement containing low concentrations of EG. At the 0.1 weight ratio, however, significant differences are obvious. Figure 1 shows micrographs taken at relatively low magnification under conditions as nearly identical as possible. In the figure, a) contains 0.04 g EG/g cement, b): 0.1 EG/cement, c): 0.2 EG/cement. At higher magnifications it is possible to find features that have appearences similar to those in a control cement.

Table 16

Percent Recovery of p-Aminomethylphenol

in Extraction with Water

	Percent Recovery			
Ratio*	12 h	24 h	7 d	28 d
1:50	94	83	51	49
1:25	101	98	63	57
1:10	102	94	85	76
1:5	101	94	87	88

*Weight ratio of pAMP to cement. Ratio of water to cement is 0.4 in each case.

However, the differences in appearance are strikingly evident in the general views at 300X. In particular, massive structures and regions of crystallinity become much less common as EG concentration increases, until finally c) bears little resemblance to the cement control. The differences between cement and a) might well go unnoticed if the other members of the series were not available for comparison. It is also worth noting that the major break in DMSO extraction behavior occurs at approximately the same concentration at which major morphological differences become obvious.

p-Chlorophenol samples

pCP samples were examined in great detail by SEM and EDX. The results for polished surfaces will be presented first. Figures 2 through 5 are micrographs of the polished sections. The 7 day old plain cement (control) is shown in Fig. 2(a). Inclusions as large results for polished surfaces will be presented first. Figures 2 through 5 are micrographs of the polished sections. The 7 day old plain cement (control) is shown in Fig. 2(a). Inclusions as large as 20 μm in diameter were observed, as shown by the arrow in Figure 2 (a). These inclusions were more resistant to polishing than the matrix phase as evidenced by their relief above the matrix. At 90 days, inclusions were still present as shown in Fig. 2(b), although they were not as well defined in the microstructure. With increasing amounts of pCP, the hardness differential decreased, thereby lessening the contrast between the matrix and inclusions when imaging was in the secondary electron mode. This trend toward uniform hardness with increasing hydration time was observed for all specimens and is likely to be a result of the gradual reaction of C_3S crystals with water forming the CSH matrix. For the 90 day old and some of the 28 day old specimens, the inclusions were only visible by backscattered electron imaging in which image contrast exists between two points when the average atomic number between the points differs. This is seen in Figs. 6 and 7.

Approximately 20 spot analyses were performed on each polished section for a total of 157 analyses. By semiquantitative analysis, atomic percentages of the EDXA detectable elements were obtained. Aluminum was omitted from these analyses because incomplete washing of the alumina polishing powder during preparation made the measured amount of aluminum unrepresentative of the hardened paste. Several typical analyses are presented in Table 17. Atomic ratios of (Ca+Mg)/Si and (Ca+Mg)/Cl were also calculated. Some of these values are listed in Table 18.

By careful examination of the SEM image just prior to EDXA, each point that was analyzed was designated an inclusion, matrix

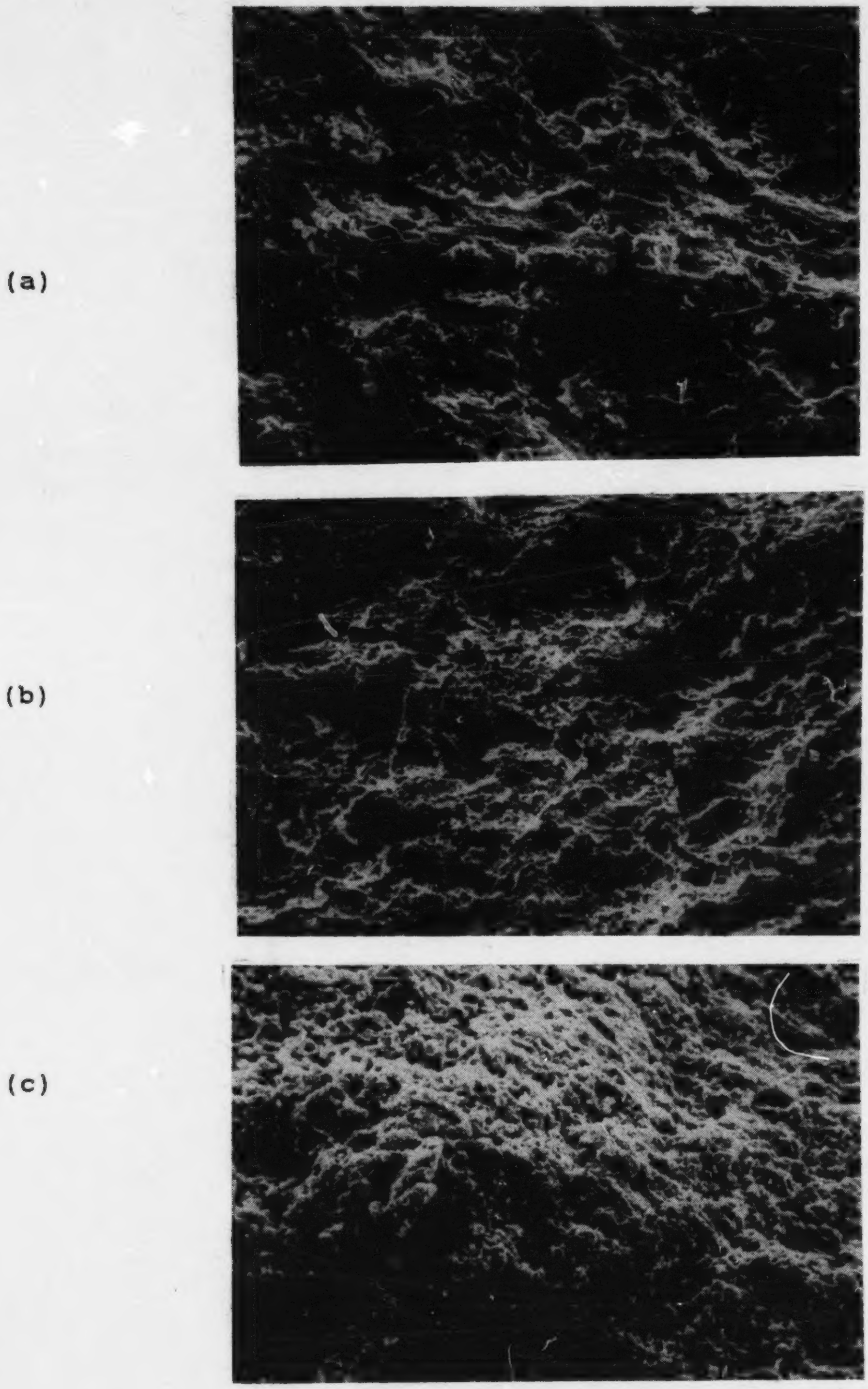
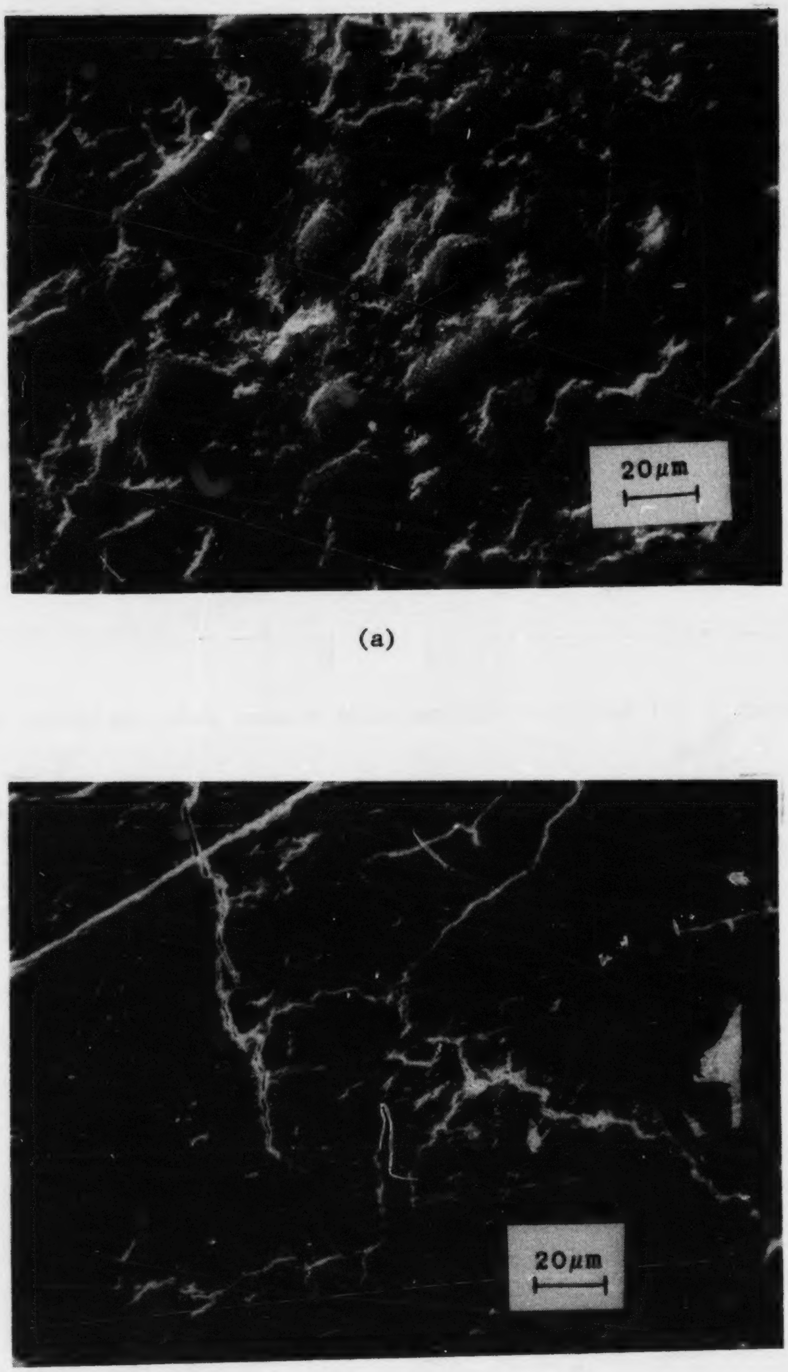


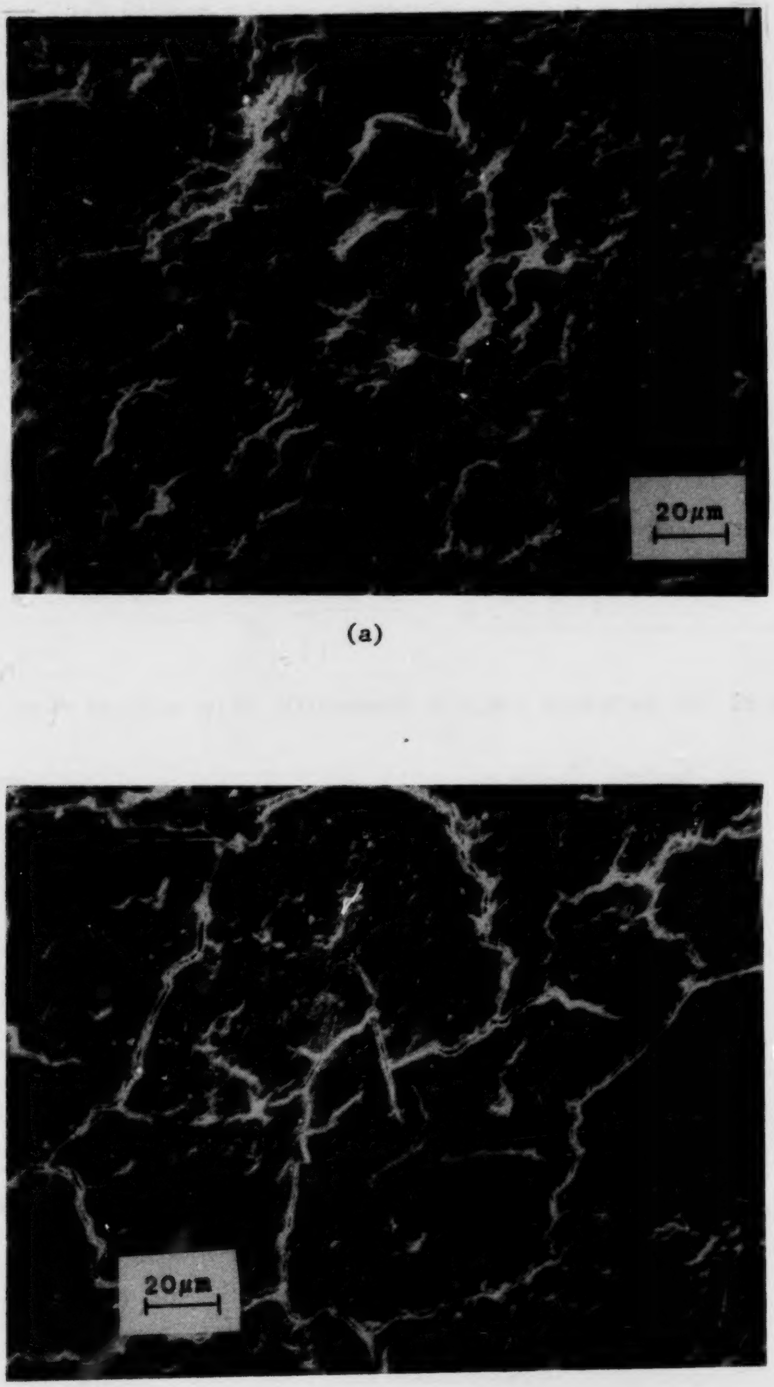
Figure 1. Fracture surfaces of samples containing (a) 0.04, (b) 0.1 and (c) 0.2 g EG/g OPC at 300X magnification.



(a)

(b)

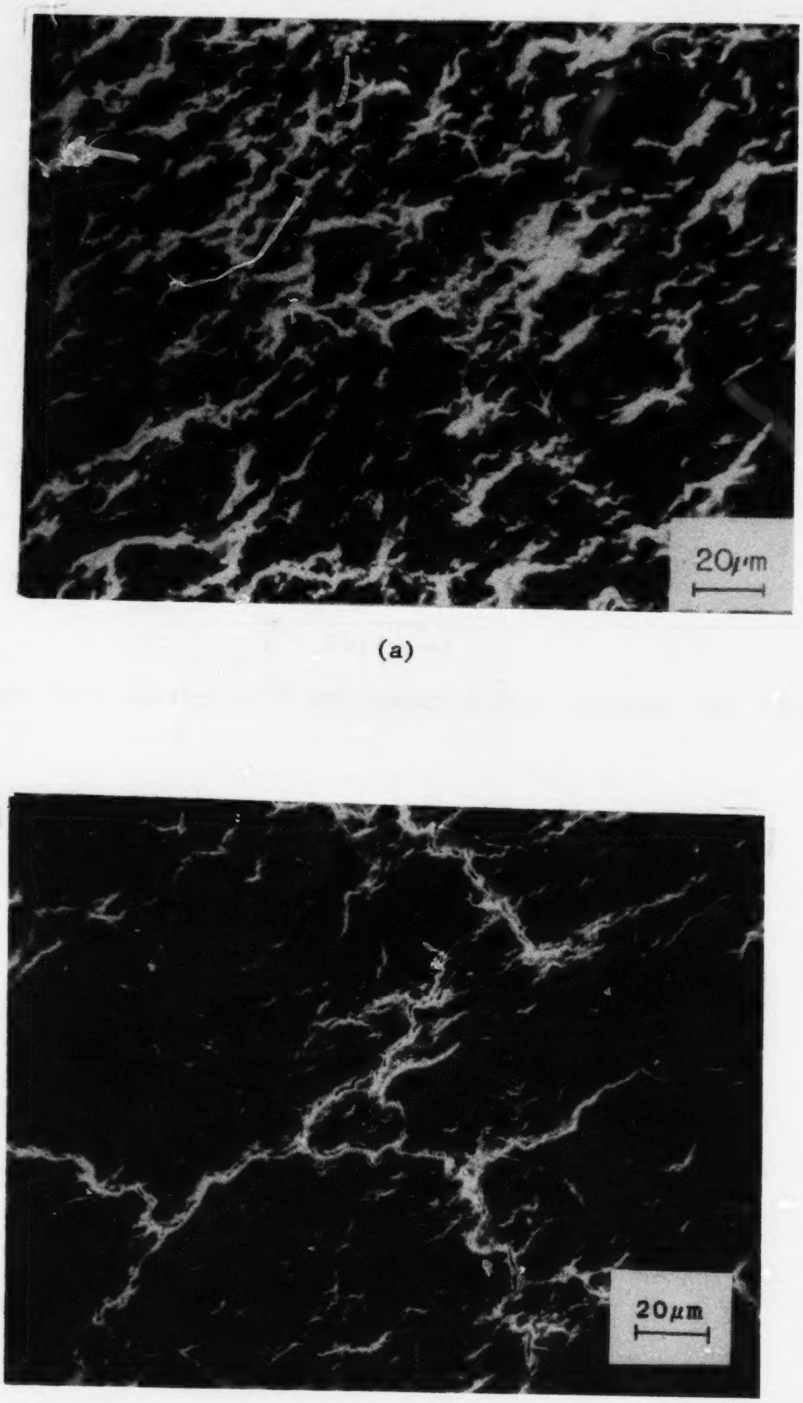
Figure 2. An uncontaminated cement thin section hydrated for (a) 7 days; (b) 90 days.



(a)

(b)

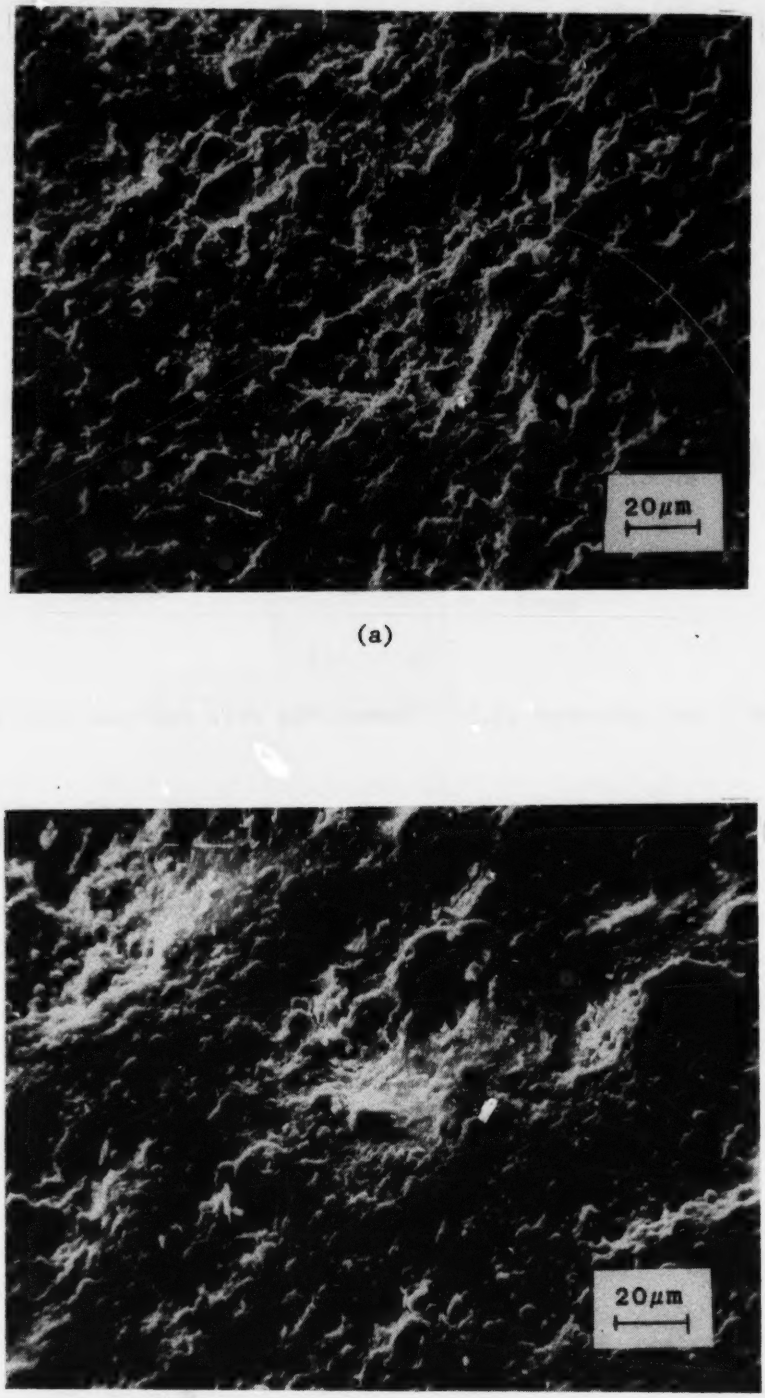
Figure 3. A cement thin section with pCP/cement = 0.04; hydrated for (a) 28 days; (b) for 90 days.



(a)

(b)

Figure 4. A cement thin section with pCP/cement = 0.1; hydrated for (a) 7 days; (b) for 90 days.



(a)

(b)

Figure 5. Cement thin section with pCP/cement = 0.2; hydrated for (a) 7 days; (b) 28 days.

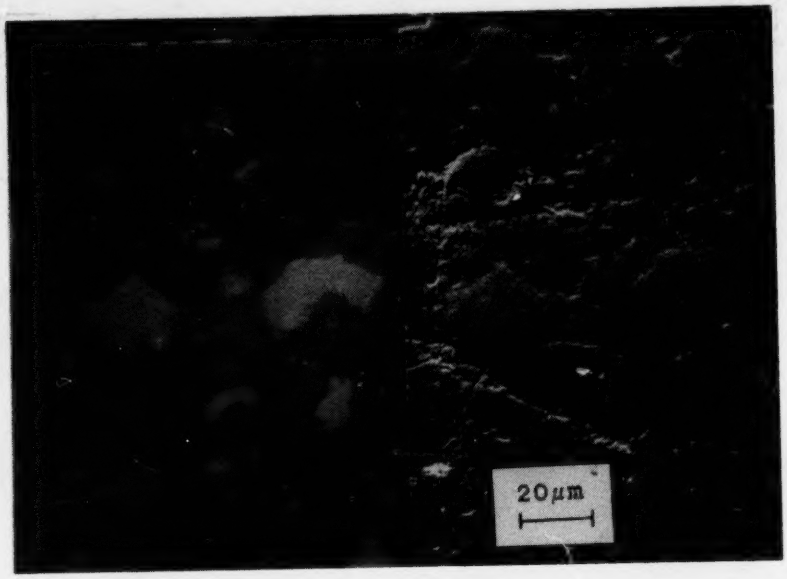


Figure 6. Cement thin section with pCP/cement = 0.04; hydrated for 90 days. A backscattered electron image is shown on the left side of the micrograph while the right-hand image is of the same field of view but imaged with secondary electrons.

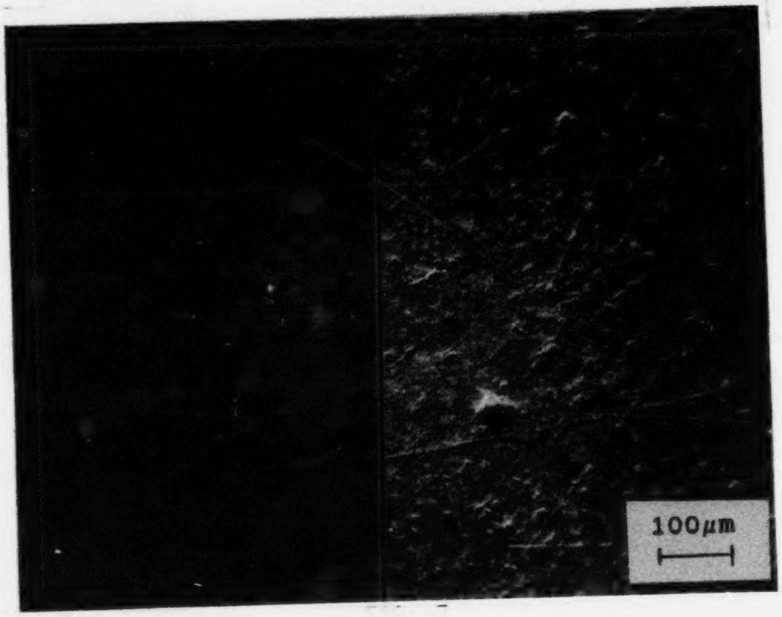


Figure 7. Uncontaminated cement thin section hydrated for 90 days; the backscattered image is shown on the left and secondary electron image on the right.

TABLE 17
Selected Elemental Atomic Percentages Obtained from Random Spot Analyses

O/C*	Morphology+	Age (Days)	Mg	Si	S	Cl	K	Ca	Fe
0	I	7	3.1	16.8	1.5	0	0.7	47.0	1.2
0	I	7	4.6	22.5	1.8	0	0.7	40.2	0.9
0	M	7	3.4	20.7	2.2	0	1.0	30.0	0.7
0	M	7	5.0	15.1	3.4	0	0.8	44.4	1.7
0	I	90	3.0	21.1	2.0	0	4.1	60.5	0.7
0	I	90	5.3	21.4	1.7	0	1.8	55.5	2.8
0	U	90	4.2	25.9	1.9	0	1.0	57.9	1.1
0	U	90	5.4	28.5	1.9	0	3.9	47.7	1.3
0.04	U	28	4.8	18.9	2.4	0.8	0.8	40.5	0.8
0.04	U	28	3.1	19.3	2.3	0.9	0.6	43.9	1.0
0.04	U	28	2.8	19.3	1.4	1.3	0.6	54.4	0.5
0.04	U	90	4.0	28.5	2.4	1.1	0.8	50.8	0.9
0.04	U	90	3.6	24.9	2.4	1.2	0.4	55.7	0.9
0.04	U	90	4.3	24.6	2.1	0.8	0.8	56.9	1.0
0.1	U	7	2.6	25.1	0.9	0.9	0.5	37.9	0.5
0.1	U	7	5.5	28.7	1.1	3.8	0.4	30.6	1.4
0.1	U	7	5.3	18.5	1.8	1.3	0.4	45.0	1.0
0.1	U	90	3.7	19.2	1.8	0.5	0.6	55.3	1.3
0.1	U	90	6.1	27.3	2.2	0.8	0.3	50.1	1.8
0.1	I	90	6.1	19.9	2.5	1.2	0.6	48.6	2.7
0.1	I	90	5.3	20.1	2.0	0.7	0.4	57.8	1.0
0.2	U	7	4.3	21.2	2.0	1.3	0.8	46.7	0.9
0.2	U	7	4.2	20.6	1.9	1.6	0.7	44.2	0.9
0.2	U	7	5.6	16.6	3.0	1.9	0.6	45.7	1.4
0.2	U	28	3.6	17.7	1.7	0.8	0.5	45.1	0.4
0.2	U	28	3.2	17.1	2.1	1.9	0.5	43.5	1.1
0.2	U	28	6.8	7.3	1.1	9.2	0.7	12.0	0.4

*O/C = Organic (pCP) to cement weight ratio.

+Morphology; I = inclusion, M = matrix, U = unknown.

TABLE 18
Selected Atomic Ratios for Random Spot Analyses

O/C *	Morphology +	Age (Days)	$\frac{(Ca+Mg)}{Si}$	$\frac{(Ca+Mg)}{Cl}$
0	I	7	2.98	0
0	I	7	2.00	0
0	M	7	2.33	0
0	M	7	2.24	0
0	I	90	3.01	0
0	I	90	2.46	0
0	U	90	2.11	0
0	U	90	3.10	0
0.04	U	28	3.50	42.41
0.04	U	28	2.97	59.45
0.04	U	28	2.97	46.65
0.04	U	90	2.48	66.37
0.04	U	90	2.13	53.90
0.04	U	90	2.49	76.78
0.1	U	7	1.62	44.96
0.1	U	7	2.15	32.00
0.1	U	7	2.13	40.32
0.1	I	90	2.93	77.41
0.1	I	90	3.14	84.44
0.1	I	90	2.58	99.41
0.1	U	90	2.69	117.07
0.1	U	90	2.92	79.66
0.1	U	90	3.40	97.90
0.2	U	7	2.41	37.25
0.2	U	7	2.32	29.30
0.2	U	7	3.10	26.80
0.2	U	28	2.75	64.37
0.2	U	28	2.01	26.92
0.2	U	28	2.33	34.04

*O/C = Organic (pCP) to cement weight ratio.

+Morphology; I = inclusion, M = matrix, U = unknown.

or unknown. The assignment was based solely on appearance in the microscope image and, therefore, the number of "unknown" points was high for the older specimens. Only three specimens (the control specimens and the 90 day old specimen containing a pCP/cement ratio of 0.1) had morphologies which would permit an easy determination of type.

If it is assumed that the inclusions are unhydrated particles, due to their size and shape, the (Ca+Mg)/Si ratio should reveal the clinker phase. Table 19 attempts to illustrate this idea for several inclusions.

From the cement oxide content analysis given in Table 1 and the known amount of pCP in each specimen, the percentages of the analyzed elements could be calculated for the sample as a whole. These values along with the mean values from the EDXA analyses are presented in Table 20.

Pearson product-moment correlation coefficients were calculated to measure the degree to which each pair of elements varied relative to one another. A correlation coefficient of unity implies a linear relationship between the two elements. Correlation coefficients between chlorine and each of the other elements are presented in Table 21.

X-ray dot maps of Cl were photographed for several areas on each polished section. All were similar to the one shown in Fig. 8.

The apparent smoothness of the polished samples increased as hydration time increased. This can be explained by a decrease in the hardness differential between the inclusions and the matrix phase(s). At least part of this phenomenon is due to dissolution of clinker phases. Other mechanisms may be explained by Diamond[18] who suggests that calcium hydroxide grows through areas where CSH has previously been deposited, thereby producing intermixing, or homogenization of the material. Increased smoothness as a function of pCP content may be explained by a reduced production of calcium hydroxide. This is consistent with Ramachandran's observations of cement containing triethanolamine[19].

Ranges about the elemental means for each specimen were determined using the student's t distribution at a 10% significance level. If a composition falls outside this range, there is a 10% chance that it is statistically different from the mean value for the sample. Each point was checked for elemental contents falling outside this range. No patterns were discerned, however, between morphology and significantly deviating contents. It may be that the data is insufficient for trends to be apparent, but there may also be wide variations of composition within the spot analyzed. Using a transmission electron microscopy equipped with an EDXA, Gars[20] in examining C_3S pastes and Lachowski and Diamond[21] in analyzing cement paste found a wide variation in the Ca/Si atomic ratio within one micrometer size particles. The area analyzed by the SEM/EDXA system is at least five micrometers across.

X-ray dot maps for Cl, such as illustrated in Fig. 8, are either inconclusive because of the inapplicability of x-ray maps

TABLE 19
Identification of Selected Inclusions by Atomic Ratios

O/C*	Age (Days)	$\frac{(Ca+Mg)}{Si}$	Probable Clinker Phase
0	7	2.98	C_3S
0	7	1.99	C_2S
0	7	2.06	C_2S
0	7	2.00	C_2S
0	90	3.01	C_3S
0	90	2.16	C_2S
0	90	3.05	C_3S
0.1	90	2.93	C_3S
0.1	90	3.14	C_3S
0.1	90	2.75	C_3S
0.1	90	2.58	C_3S

*O/C = Organic (pCP) to cement weight ratio.

TABLE 20
Comparison of Calculated and Experimentally Determined Values of Elemental Content

ELEMENT	CONTROL			O/C = 0.2		
	CALC.	7 DAY	90 DAY	CALC.	7 DAY	28 DAY
Mg	4.6	4.2	4.6	4.3	4.7	4.3
Si	19.3	20.1	23.8	17.9	19.3	16.3
S	2.3	1.9	2.0	1.9	2.3	1.6
Cl	-	-	-	8.2	1.7	2.3
K	0.6	0.7	2.5	0.7	0.6	0.5
Ca	65.9	46.2	56.3	60.5	44.2	37.0
Fe	1.7	1.1	1.1	1.6	1.2	0.8

ELEMENT	CONTROL			O/C = 0.2		
	CALC.	7 DAY	90 DAY	CALC.	7 DAY	28 DAY
Mg	4.4	4.2	4.9	4.6	3.5	4.0
Si	18.7	23.0	22.2	19.2	19.5	26.8
S	2.0	1.5	1.9	1.0	1.8	1.9
Cl	4.3	1.6	0.9	1.7	1.0	0.9
K	0.7	0.4	0.6	0.8	0.7	1.1
Ca	63.0	43.4	54.3	64.6	49.6	52.3
Fe	1.7	1.1	1.3	1.7	0.8	1.3

TABLE 21
Correlation Coefficients Relative to Chlorine

ELEMENT	O/C = 0.2		O/C = 0.1		O/C = 0.04		
	7 DAY	28 DAY	7 DAY	90 DAY	28 DAY	90 DAY	ALL
Mg	0.25	0.71	0.24	0.06	0.08	-0.41	0.30
Si	-0.27	-0.74	-0.06	0.34	-0.27	0.52	-0.27
S	0.34	-0.54	-0.19	0.02	0.42	-0.08	-0.19
K	0.41	-0.08	-0.10	0.33	-0.20	0.14	-0.03
Ca	-0.41	-0.90	-0.24	-0.12	0.03	-0.57	-0.70
Fe	-0.24	-0.22	-0.16	-0.24	0.18	0.35	-0.14

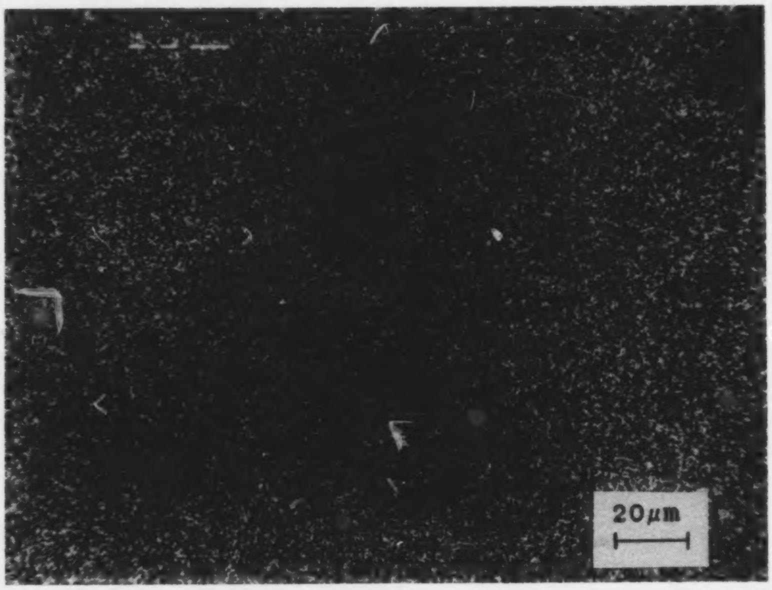


FIG. 8

Chlorine x-ray dot map of the area shown in Fig. 4(a) for concentration less than 10%[22] or they are indicative of an even distribution. Electron microprobe analyses described by Roy et. al.[23] conducted on the same specimens studied herein support the even distribution hypothesis. Contradictory to this evidence is the drastic increase in the mean value and standard deviation of (Ca+Mg)/Cl as hydration time increased for all pCP concentrations. This suggests that pCP is concentrating in certain areas as hydration proceeds. Grouped by morphology, this ratio is higher in the inclusions than the matrix.

Judging by the shape, hardness, and content of the inclusions, it is presumed that these are unhydrated cement particles. Although there was less Cl associated with these particles, it is important to note that Cl was detected on the relatively large (approximately 20 μm across) particles. This suggests a possible interaction between pCP and the unhydrated phases.

In summary, the study of eight thin sections suggested a decrease in the hardness differential between inclusions and matrix phases with increasing hydration time as well as increasing parachlorophenol concentration. From areas on these thin sections, 157 random spots were analyzed for elemental composition.

X-ray dot maps and electron microprobe analyses of Cl on all specimens examined indicates an even distribution of pCP within the samples. However, mean and standard deviation values for each specimen of (Ca+Mg)/Si increased as hydration time increased suggesting that the pCP is migrating unevenly within the sample as the hydration proceeds. This ratio is higher in the inclusions as compared to the matrix. This is reasonable if it is assumed that the inclusions are mainly unhydrated cement particles which have a higher calcium concentration than the matrix material, primarily CSH gel. The detection of chlorine, although in a lesser amount than in the matrix, in the relatively large (approximately 20 μm across) particles implies an interaction between pCP and the unhydrated phases.

Fracture surfaces of pCP/cement samples have also been studied in detail by SEM. A number of micrographs have been included here to thoroughly document the observations. Too many microscopic studies have resulted in papers which include only a few micrographs thus making it very difficult to apply the results to other studies. The descriptions of the micrographs on the following pages are listed in order of increasing hydration time. They are further subdivided by increasing pCP content.

12 Hour Hydration

Specimens with an organic/cement ratio (OC) of 0, 0.04 and 0.1 are shown in Fig. 9. The specimen with O/C=0.2 was liquid after 12 hours and was, therefore, omitted.

On the surface of the control specimen (O/C=0), large irregularly shaped particles, 20 to 50 μm across, are partially covered with clusters of acicular hydration product roughly 0.5 μm in diameter (Fig. 9 (c)). The large particles are likely to be unhydrated cement clinker, judging by their size and irregular

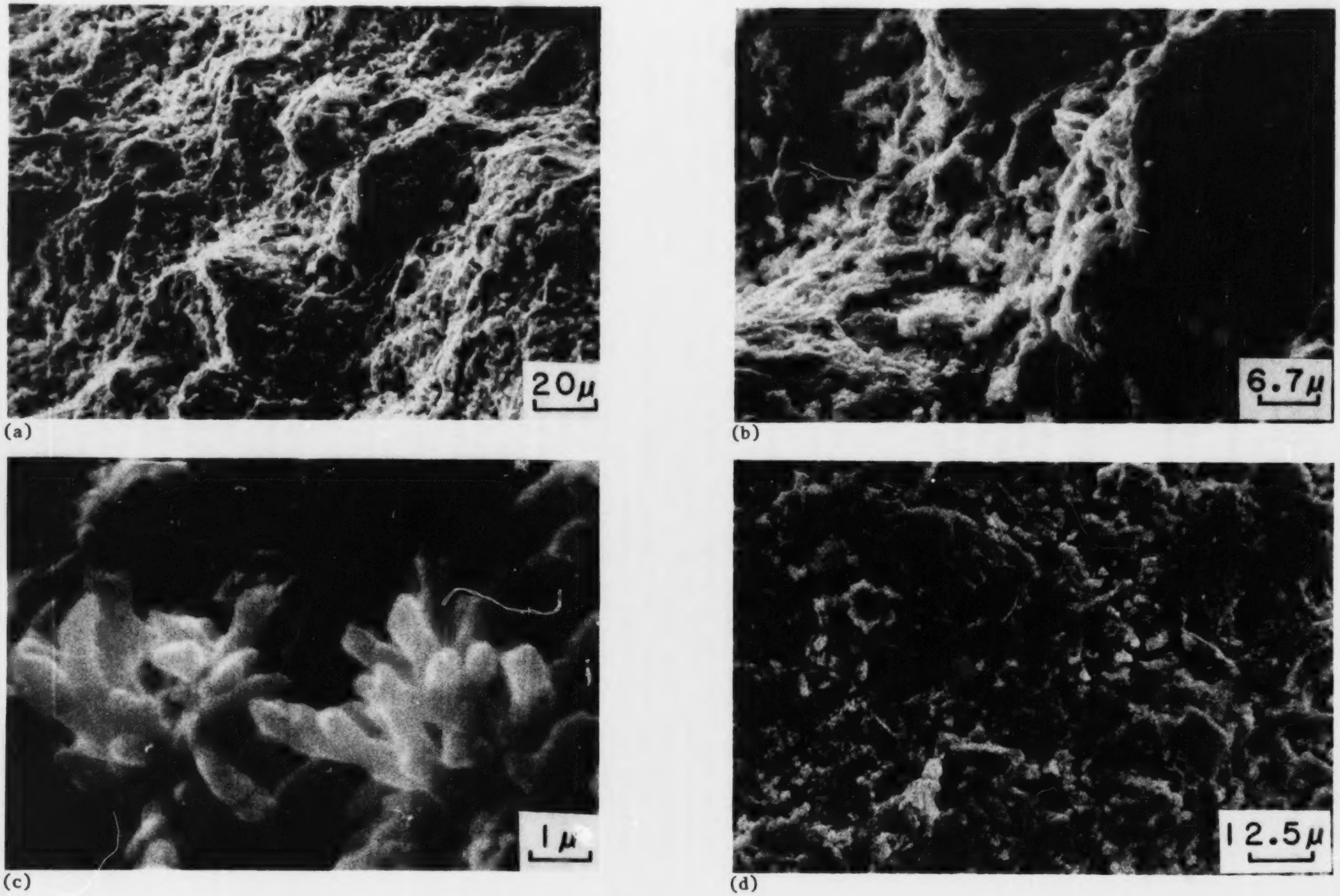
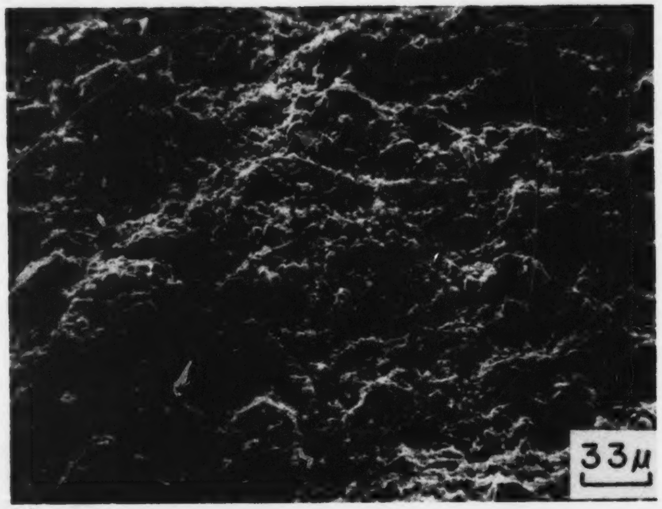
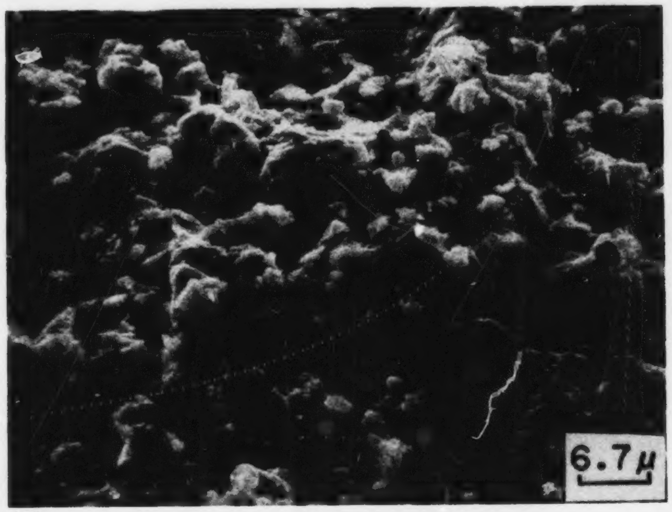

20μ
(a)
6.7μ
(b)
1μ
(c)
12.5μ
(d)

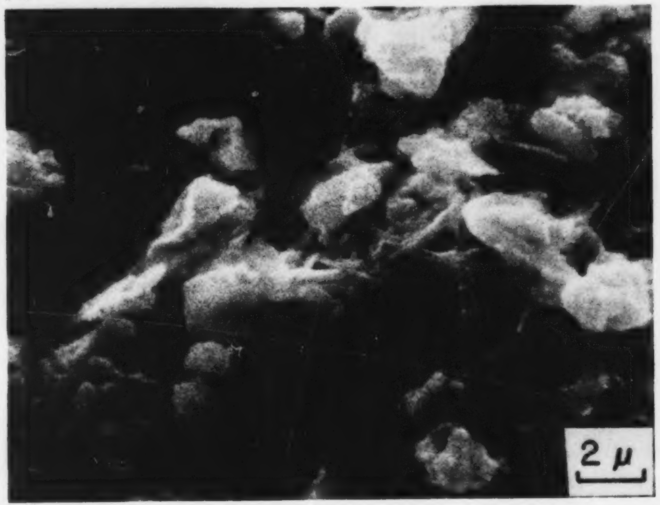
Figure 9. Scanning electron micrographs of cement samples after hydration for 12 hours; O/C ratios: (a) through (c), 0; (d), 0.04; (e) through (g), 0.1.



(e)



(f)



(g)

Figure 9. Scanning electron micrographs of cement samples after hydration for 12 hours; O/C ratios: (a) through (c), 0; (d), 0.04; (e) through (g), 0.1.

shape. These large particles give the surface a slightly denser appearance than those observed at later hydration times. The clusters of acicular material resemble ettringite, which is the early stage hydration product of tricalcium aluminate.

The O/C=0.04 specimen appears more porous (see arrow in Fig. 9 (d)) than the control. This could be due to a smaller amount of hydration product having been formed, a less bulky hydration product, or greater dissolution of the large, irregular particles.

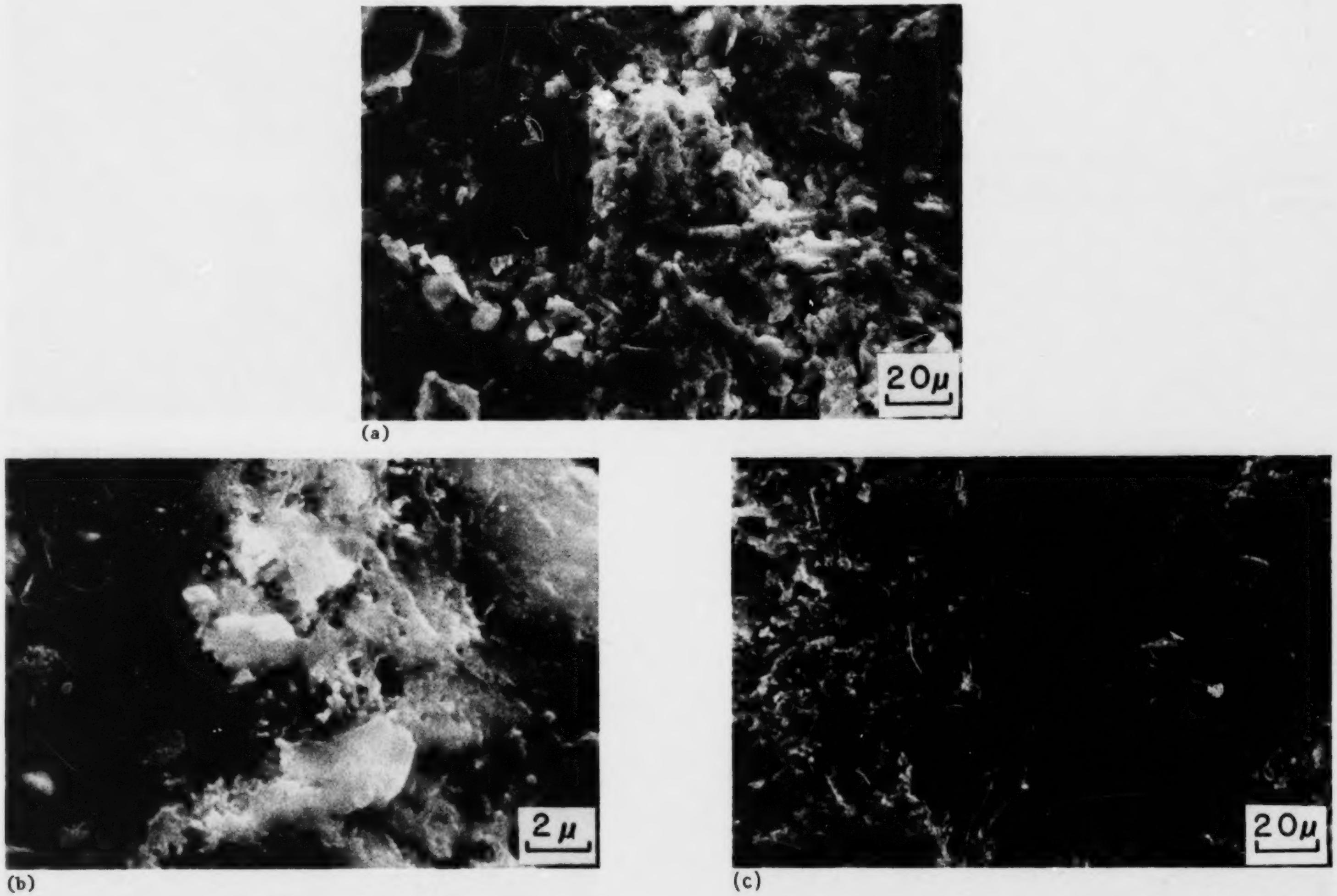
The O/C=0.1 specimen also revealed a more porous surface than the control. The small, brighter particles especially evident in Fig. 9(g) are believed to be hydration product. Instead of acicular clusters as found in the control, stacks of irregularly shaped plates with sharp, flat edges and thin strips approximately 2 to 3 μm long by 0.25 μm wide are observed. They do not seem to cover, or grow from, the large particles, but are free-standing. The large particles, probably unhdrated clinker, are not as large in this specimen as is the control. This could be due to greater dissolution of the large particles in the specimen.

24 Hour Hydration

Fig. 10 shows specimens with an O/C=0, 0.04 and 0.1. Fig. 10(a) and (b) represent the microstructure of the control specimen after hydrating for 24 hours. These micrographs, however, were taken after the fractured specimen had been stored for one year in a dessicator. It is suspected the specimen has undergone further reaction during storage because of the inconsistent appearance of Figs. 10(a) and (b) when compared to the 12 hour and the 7 day old control specimens in Figs. 9 and 11, respectively. The surface shown at lower magnification is much denser than the 12 hr. and 7 day controls. The smooth dark area approximately 15 by 24 μm, to the left of center in Fig. 10(a), gives the surface a polished look. At higher magnifications (Fig. 10(b)), the appearance is more porous, but a flattened appearance is also noted. Rods, approximately 0.1 micrometers in diameter, shown by the arrow in Fig. 10 (b), are randomly oriented and bridge the flattened areas.

In Fig. 10(c), the porosity of the O/C=0.04 specimen has decreased slightly. Large, irregular particles are still observed; however, there is less space between them. Hydration product of uncertain type at this magnification is probably responsible.

The O/C=0.1 specimen exhibits a denser surface after 24 hours hydration than it did after 12 hours. This can be seen by comparing Fig. 10(d) and Fig. 9(e). The irregularly shaped stacked plates observed in the 12 hour specimen (Figs. 9(f) and 9(g)) are present in Fig. 10(e) (see arrow), although they now have rod-like crystals growing at 90° to the flat surface of the plates. The rods are similar in size and shape to the acicular crystals on the 12 hour control shown in Fig. 9(c). The rods observed in Fig. 10(e), however, are randomly scattered rather than clustered. The thin strips seen in Fig. 9(g) are no longer observed.

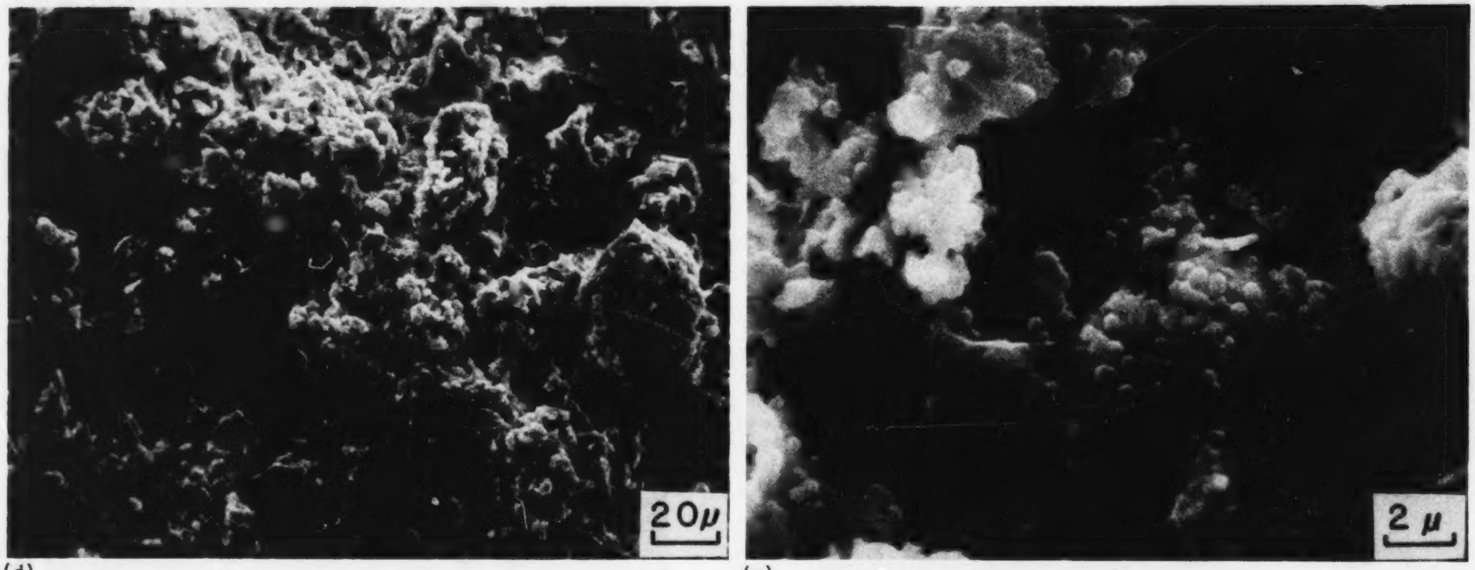


(a)

(b)

(c)

Figure 10. Scanning electron micrographs of cement samples after hydration for 24 hours; O/C ratios: (a) and (b), 0; (c) 0.04; (d) and (e), 0.1.



(d) (e)

Figure 10. Scanning electron micrographs of cement samples after hydration for 24 hours; O/C ratios: (a) and (b), 0; (c), 0.04; (d) and (e), 0.1.

7 Day Hydration

Fig. 11 shows specimens with O/C=0, 0.04, 0.1 and 0.2, respectively. The control specimen in Fig. 11(a), at low magnification, resembles the same specimen after 12 hours (Fig. 9(a)), except that the large particles have decreased in size. At high magnification (Fig. 11(b)), a bright material covers the surface of irregularly shaped particles, which could be the remnants of unhydratedclinker. The material covering the surface is not resolved clearly at this magnification and may be calcium silicate hydrate gel, according to its form and size.

As shown in Fig. 11(c), the surface of the specimen with O/C=0.04 has densified greatly. Particles that can be resolved have a more rounded appearance than at the earlier ages where angular edges were seen. At higher magnification (Fig. 11(d)), the surface consists of many circular rods approximately 0.2 μm in diameter. Some are oriented in the same direction (left half of Fig. 11(d)) and others are randomly oriented (right half of Fig. 11(d)).

Fig. 11(e) shows the O/C-0.1 specimen after hydrating for 7 days. It has few porous areas. The surface is rough and, apparently, consists mostly of a single solid rather than an amalgam of many particles.

Figs. 11(f) and 11(g) are micrographs of the specimen with O/C=0.1. The porosity and particle morphology is similar to the O/C=0.1 specimen after 12 hours of hydration (Figs. 9(e) and (f)), particularly the two particles seen near the center of Fig. 11(f). As suggested earlier, these are probably unhydrated cement clinker because of their large size and irregular shape.

28 Day Hydration

Fig. 12 shows micrographs of specimens with O/C=0, 0.04, 0.1 and 0.2. The control specimen exhibits a surface which has become overgrown with the minute projections identical to those noted on the 7 day old control specimen. Very thin, curled plates have also appeared at various locations as shown in the lower right portion of Fig. 12(b).

In comparison to the control, all of the specimens containing pCP have very dense surfaces at this stage. The specimen with O/C=0.04, shown in Fig. 12(c), is essentially identical to the same specimen after 7 days of hydration shown in Fig. 11(c).

In Fig. 12(d), the O/C=0.1 specimen has a rough surface which appears to be a single mass, as was observed in Fig. 11(e) for the 7 day specimen. However, small spherical particles about 0.5 μm in diameter now cover the surface. Areas of rough, needle-like growths, such as the one in the center of Fig. 12(d) have also appeared.

Fig. 12(e), the O/C=0.2 specimen strongly resembles Fig. 11(e), which was the O/C=0.1 specimen after 7 days of hydration. The surface in Fig. 12(e) is rough, continuous, and dense. In Fig. 12(f), the surface is covered with spherical particles of ap-

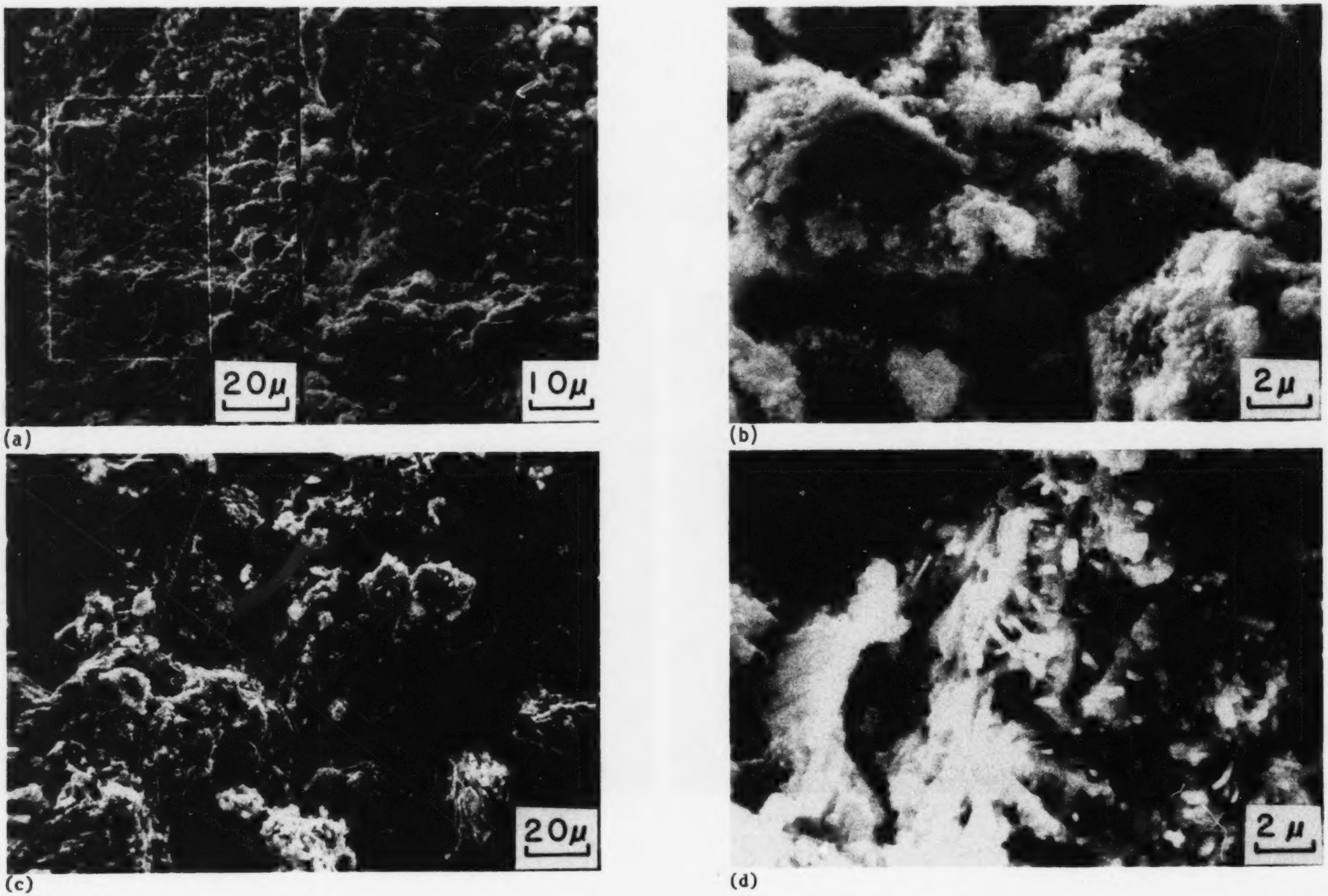

20μ
10μ
(a)
2μ
(b)
20μ
(c)
2 μ
(d)

Figure 11. Scanning electron micrographs of cement samples after hydration for 7 days; O/C ratios: (a) and (b), 0; (c) and (d), 0.04; (e), 0.1; (f) and (g), 0.2.

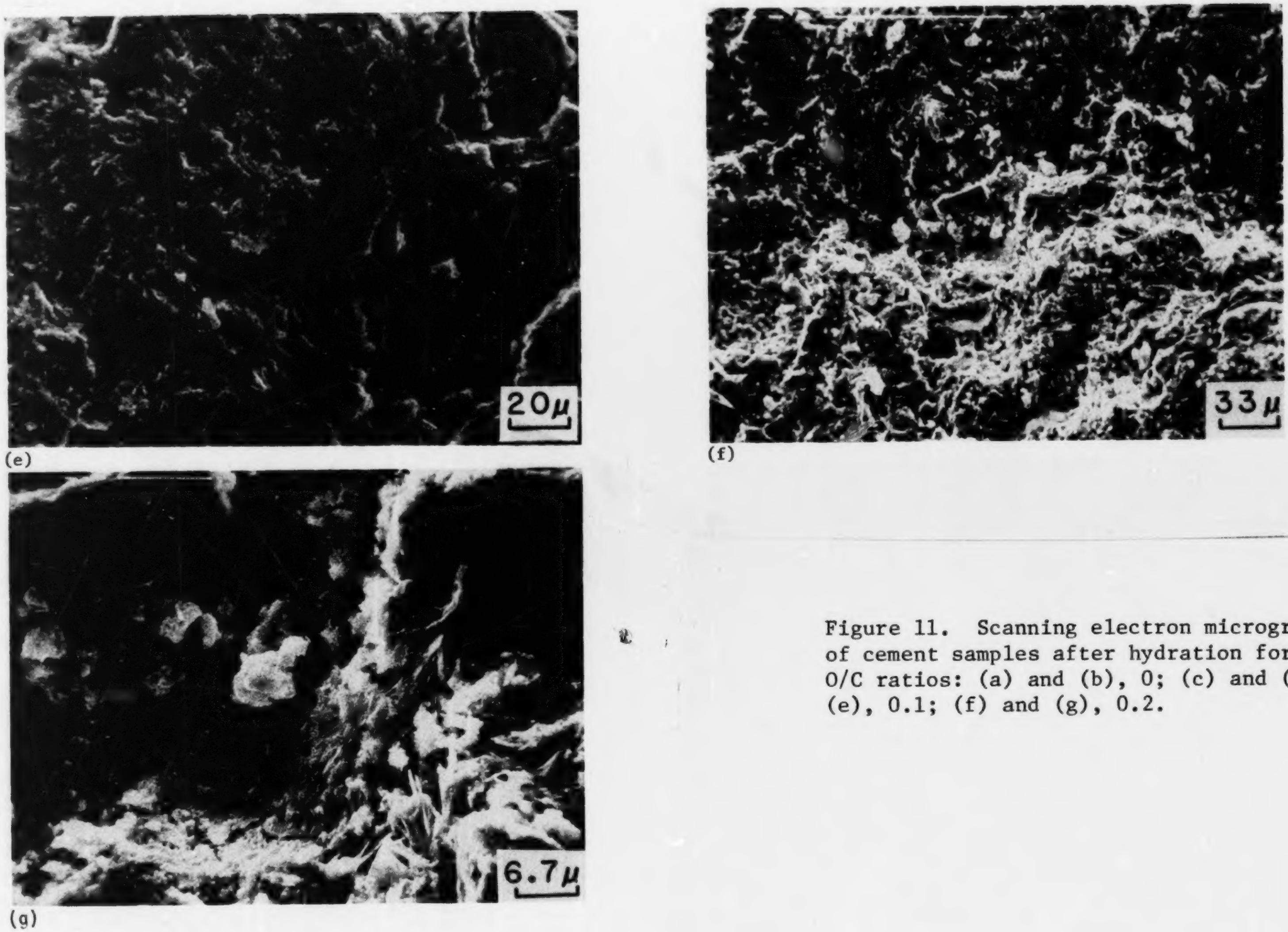

20μ
(e)
33μ
(f)
6.7μ
(g)

Figure 11. Scanning electron micrographs of cement samples after hydration for 7 days; O/C ratios: (a) and (b), 0; (c) and (d), 0.04; (e), 0.1; (f) and (g), 0.2.

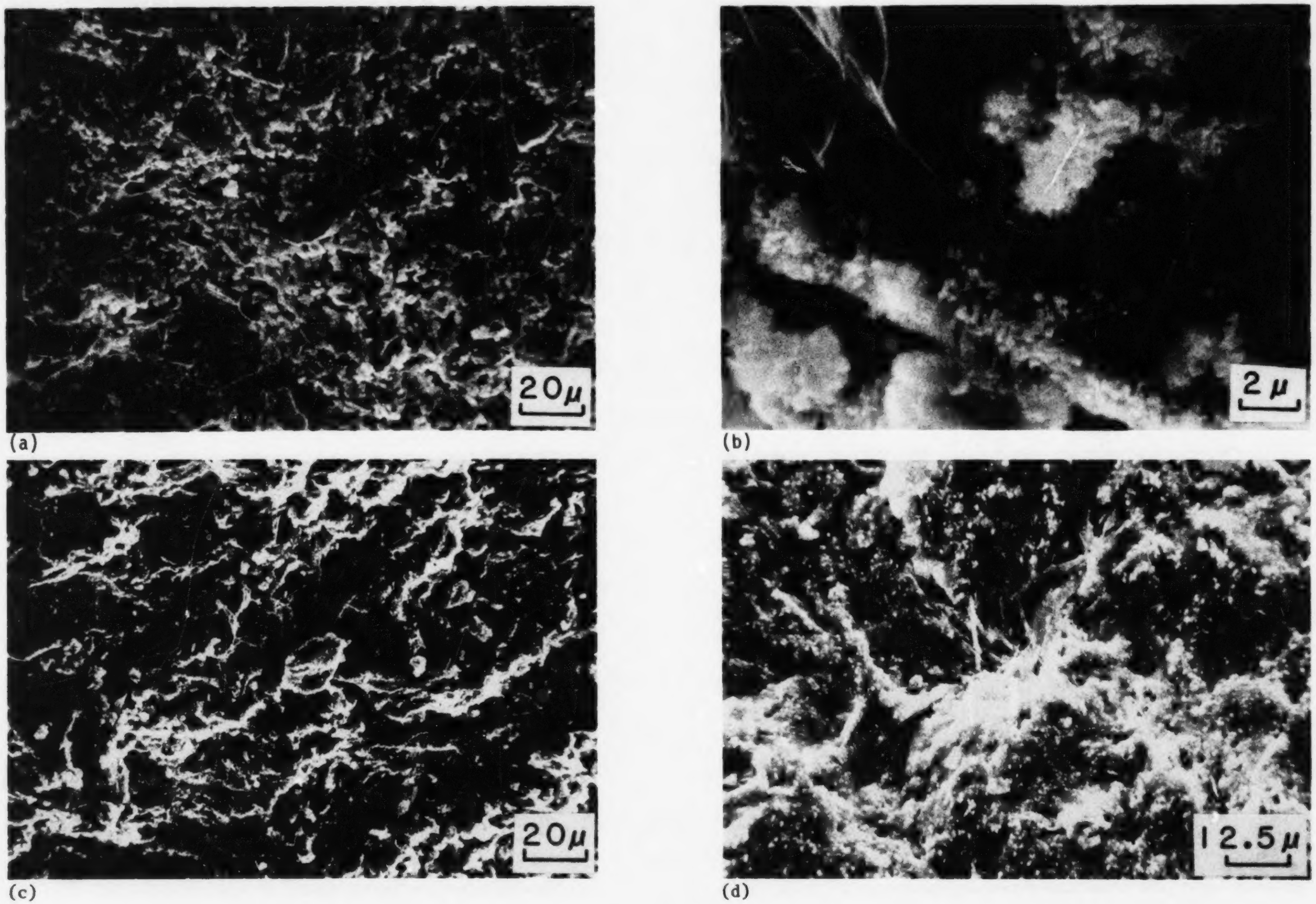
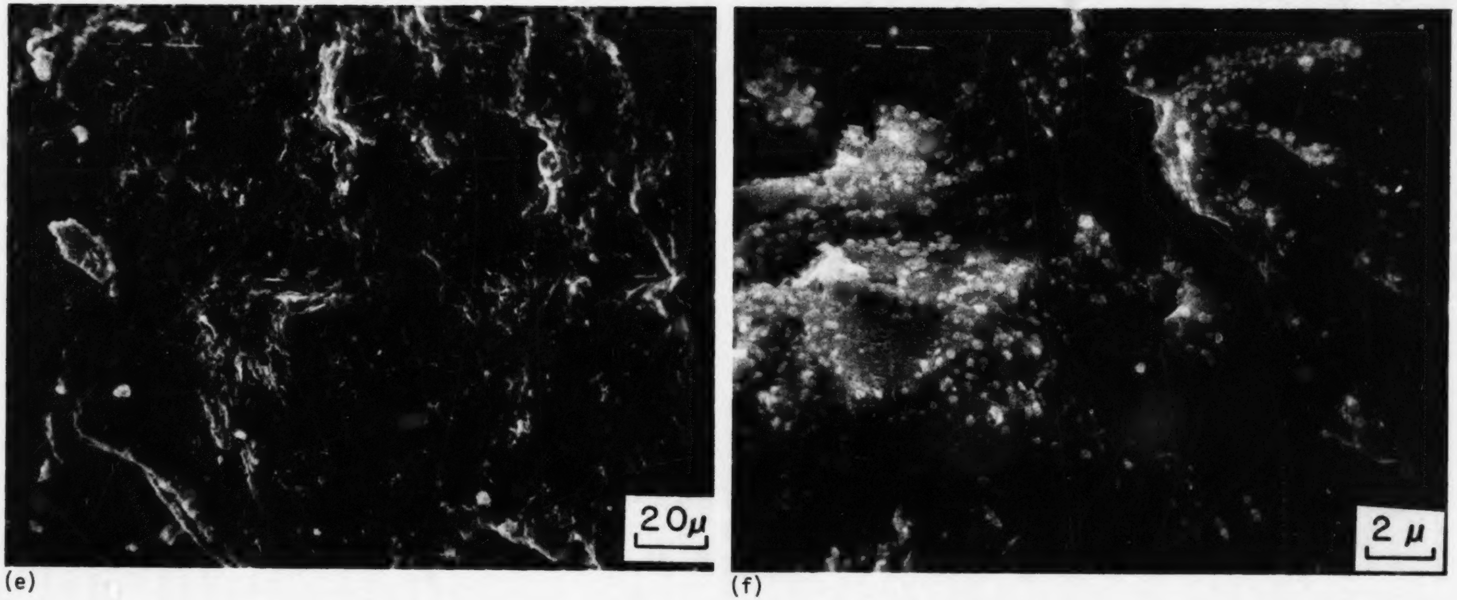

20μ
(a)
2 μ
(b)
20μ
(c)
12.5μ
(d)

Figure 12. Scanning electron micrographs of cement samples after hydration for 28 days; O/C ratios: (a) and (b), 0; (c) 0.04; (d), 0.1; (e) and (f), 0.2.



(e)
(f)

Figure 12. Scanning electron micrographs of cement samples after hydration for 28 days; O/C ratios: (a) and (b), 0; (c), 0.04; (d), 0.1; (e) and (f), 0.2.

proximately the same size as those observed on the surface of the O/C=0.1 specimen in Fig. 12(d).

Trends in microstructural development noted above can be compared to other studies of cementitious material containing admixtures. Ramachandran[24] reported that the addition of calcium chloride (a set accelerator) to tricalcium slicate paste (the major component of Type I Portland cement) increased the surface area within the tricalcium silicate. Massazza[25] also noted an increase in specific surface area of tricalcium silicate paste containing calcium chloride or triethanolamine, an organic set accelerator. Evidence of increased surface area in the present study is the angular morphology found in pCP-containing specimens (especially after 12 and 24 hour hydration) as compared to the rounded morphology of the control specimens plus the overall smaller particle sizes in the pCP-containing specimens as compared to the controls atg 12 and 24 hours.

Another noticeable trend was the change in hydration product morphology for the pCP-containing specimens when compared to the controls. Clusters of acicular products in the control were replaced by randomly oriented rods, stacks of irregularly shaped angular plates, and thin strips or rods. Ramachandran (1971) noted the morphology of calcium silicate hydrate changed from needle-like to platy with the addition of calcium chloride to tricalcium silicate paste. In a study by Milestone, sugar and sugar acids added to tricalcium silicate paste were found to alter the morphology of calcium silicate hydrate from acicular to flaky[26].

In summary, fractured surfaces of specimens containing pCP revealed angular grain morphology in the early stages of hydration (up to 7 days) followed by apparent densification, to a relatively non-porous surface. Small (<0.5 μm) spherical particles coating the exposed surfaces of contaminated specimens were also observed. In contrast, the control fracture surfaces exhibited a progressive covering of the apparently unhydrated grains with an acicular hydration product. At 28 days, the control fracture surface was still relatively porous with a fairly homogeneous surface of an intermixture of small discrete grains and mostly acicular growth on and between the grains.

The alteration of hydration products suggests a chemical interaction between cement and pCP. If a new phase incorporating the pCP molecule is forming, the stability of this phase will determine the leachability of the solidified mixture.

TEM OF ETHYLENE GLYCOL AND p-BROMOPHENOL SAMPLES

Control Cement Samples

Various morphologies of CSH were observed including fibrous, needle, tubular, and aggregates of small irregular plates. Analyses of many diffraction patterns indicate that although the morphologies differ, the crystal structures are similar with d-spacings of approximately 0.3, 0.28, and 0.18 nm. An example is shown in Fig. 13. This is consistent with previously reported

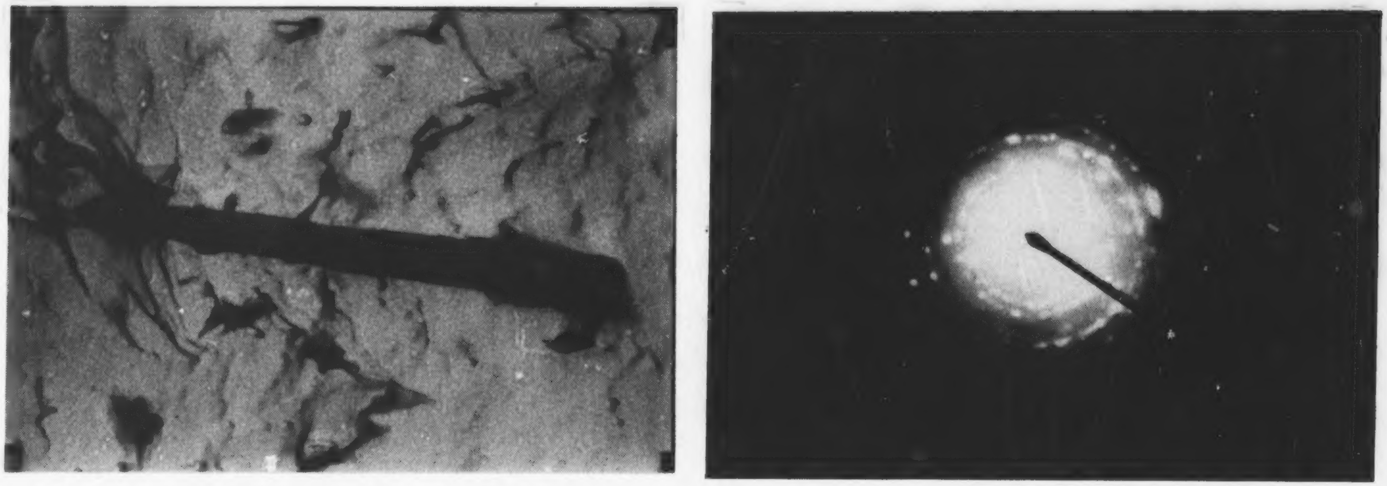


Figure 13. CSH in a pure cement aged for four months. Although a needle or rod-like morphology is exhibited, the diffraction pattern reveals a polycrystalline structure.

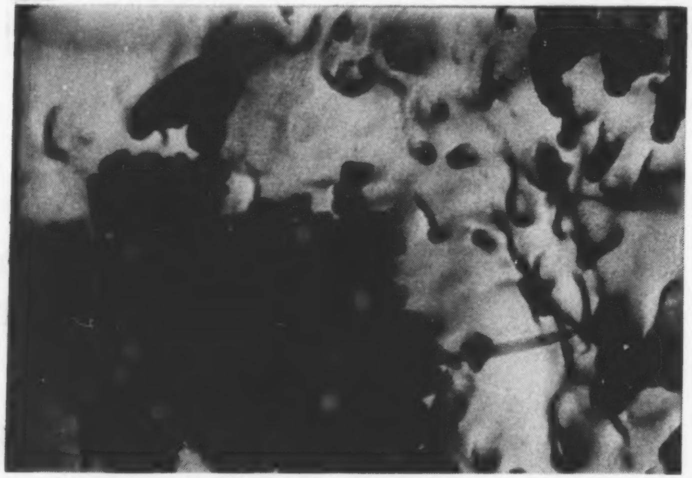


Figure 14. Polycrystalline CSH in pure cement aged for one month. Analysis of the diffraction pattern reveals a phase with d-spacings similar to the afwillite mineral.

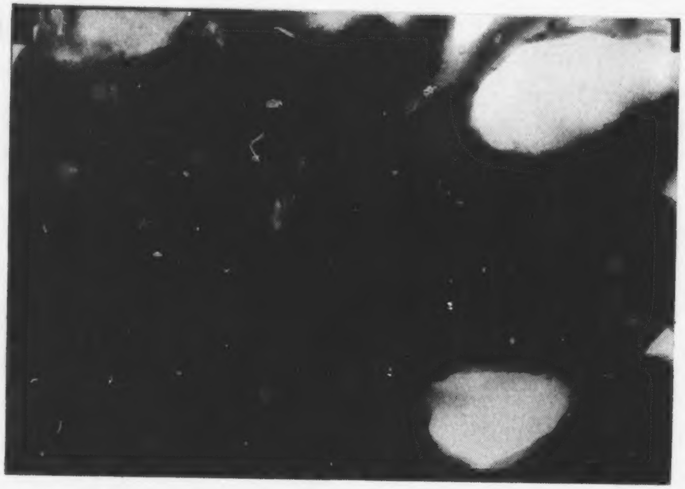


Figure 15. Crumpled foil morphology in CSH in pure cement aged four months.

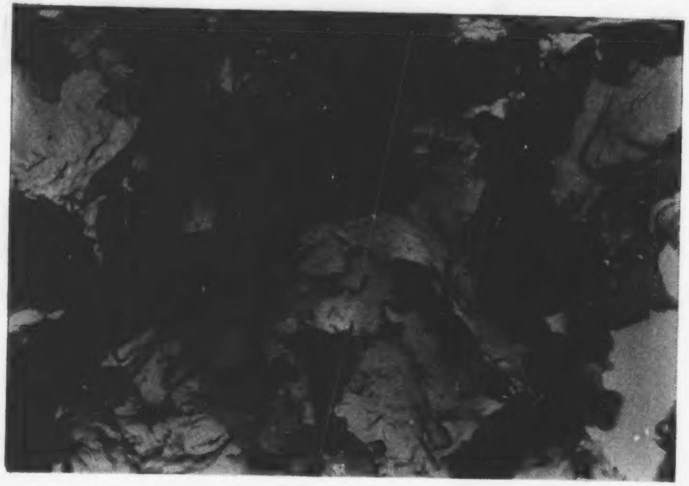


Figure 16. An amorphous phase found in ethylene glycol-containing cement aged for six months; the organic/cement (O/C) ratio was 0.1.

work.

In some cases, different diffraction patterns for CSH material were observed. For example, Figure 14 is a diffraction pattern from a specimen with d-spacings of 0.32, 0.28, and 0.16 nm. This structure is similar to afwillite. Similarly, the particle shown in Figure 15 exhibits a crumpled foil morphology with d-spacings of 0.31, 0.29, and 0.19 nm.

Cement Containing Ethylene Glycol

In cement containing ethylene glycol, the morphology and tobermorite structure of the CSH has been significantly modified. This is consistent with x-ray diffraction studies of the same material[27] where the major peak was weakened and broadened. In some specimens observed in the present work, the surface appeared "glassy" and surrounded by blocky amorphous particles. This is seen in Figure 16. In most other regions, however, CSH appeared as spherical particles embedded in an amorphous material. Some aggregates of spherical particles were amorphous and others crystalline. A variety of morphologies, each exhibiting the afwillite structure with d-spacings of 0.33 and 0.2 nm, were also observed.

Another crystalline structure was frequently observed in the ethylene glycol cement mixtures. The structure was crystalline with d-spacings of 0.208, 0.205, 0.201, 0.12, 0.115, 0.103 and 0.1 nm. Morphologies were either aggregates of spherical grains, single irregular plates, or thin flakes. Similar structures were also observed in the pure cement samples, but not to the extent seen in ethylene glycol samples.

Small crystals (15-60 nm) with a cubic structure were also observed. This structure has not been reported in pure cement and may be a reaction product of C_3A and ethylene glycol.

Figure 17 shows a $Ca(OH)_2$ crystal. The diffraction pattern shows the characteristic hexagonal structure, however, the diffraction spots are diffuse and tend to form a ring pattern. This suggest that the CSH/ethylene glycol is bonded with the $Ca(OH)_2$ forming a thin layer.

Cement Containing p-Bromophenol

The morphologies of the phases contained in cement containing p-bromophenol were also observed to differ from those in hydrated pure cement. Most of the phases appeared as spherical particle aggregates as shown in Figure 18. The number of amorphous aggregates also increased.

The degree of crystallinity of the CSH structure decreased with the addition of pBP. Large particles having d-spacings characteristic of the CSH(II) structure were observed; however, the particles retained the shape of the original cement clinker grains. This may imply that the hydration process in this material is different from hydration in the pure cement. Scanning electron microscopy observations of the same material shows that there are

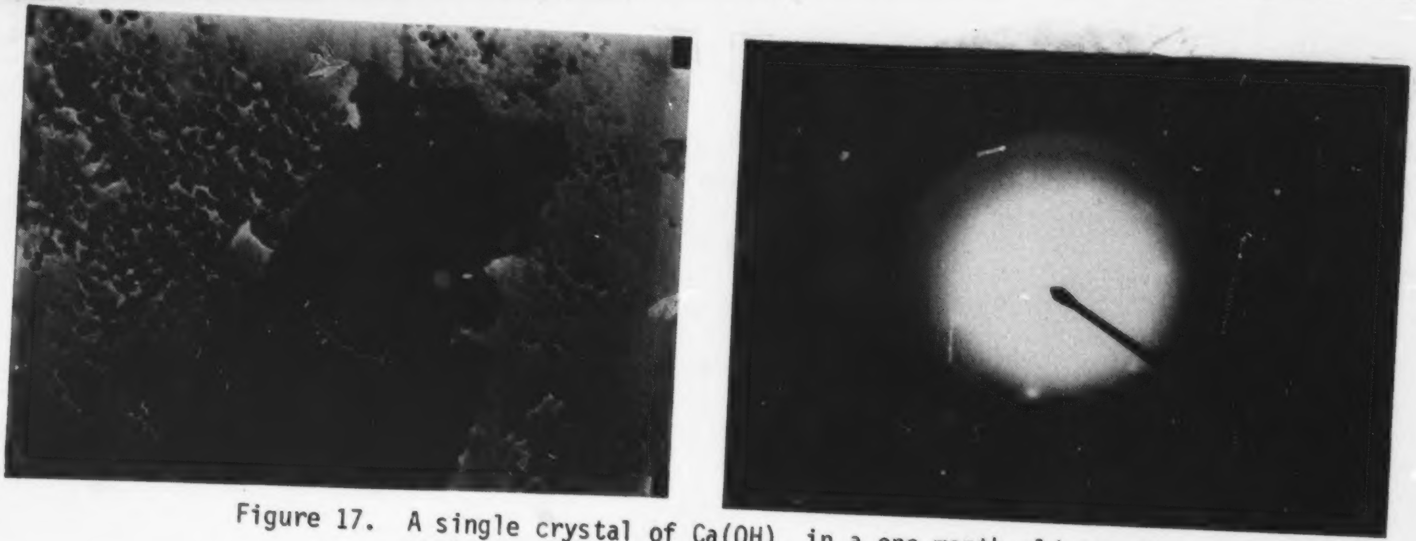


Figure 17. A single crystal of $Ca(OH)_2$ in a one month old cement containing ethylene glycol; O/C = 0.1.

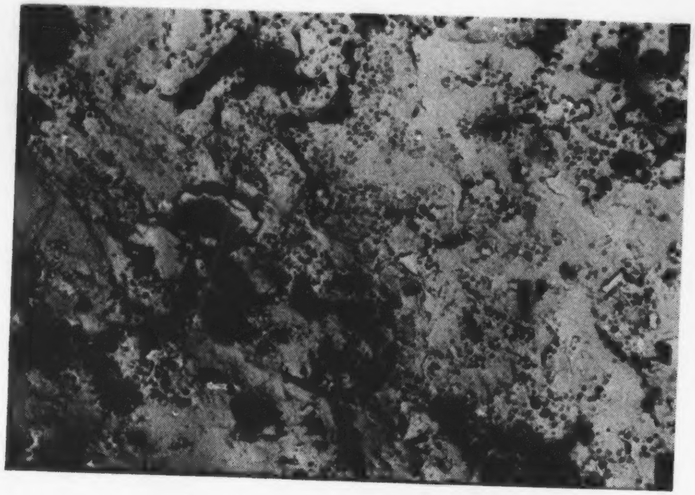


Figure 18. Crystalline spherical aggregates of CSH in cement containing *p*-bromophenol; O/C = 0.1; age = 6 months.

more large distinguishable particles in the pBP containing material[28].

It was observed that in many CSH regions, the aggregate morphology was unstable under the influence of the electron beam. The particles bubbled significantly, a phenomenon not observed in either the pure cement samples or the cement containing ethylene glycol. Possibly the pBP, or derivatives of it, were incorporated in the CSH structure, forming an unstable and volatile material. The diffraction patterns only showed a single diffuse ring with a d-spacing of approximately 0.29 nm, as illustrated in Figure 19. Similarly, several $Ca(OH)_2$ and $Mg(OH)_2$ crystals were observed. The crystals appeared streaked and diffuse, possibly due to the incorporation of pBP.

Summary of TEM Work

During the course of hydration, a variety of morphological types of CSH have been observed by researchers. Several classifications have been proposed based on SEM and TEM studies. Unfortunately, the compositional and structural differences between these types have not been well defined in the literature. Midgley[29] suggests that CSH may occur in set Portland cement in three forms: (1) fibrous material which sometimes gives diffuse diffraction patterns showing 0.305, 0.208, and 0.18 nm d-spacing of the tobermorite phase; (2) irregular masses of small, distorted plates often giving a single diffuse ring at 0.29-0.3 nm in an SAD pattern; and (3) crumpled foils where no structure was mentioned.

In general, the CSH structure is an amorphous solid body filled with small particles with a variety of morphologies, some having the same crystal structures. In this study, the tobermorite structure is observed to be the major crystal structure in CSH. In addition, this study supports Taylor's model[30] that only subcrystalline order exists in the neighborhood of small fragments of Ca-O layers in the CSH structure. The subcrystalline order extends only several hundred nm.

The major conclusions of the present study are as follows:

1. The dominant crystal structure of the CSH in pure cement is tobermorite, but with various morphologies.
2. The addition of EG or pBP to cement changes the morphology of the CSH and its crystal structure. Aggregates of small grains are the primary morphology and the amount of tobermorite structure has greatly decreased. In addition, various crystal structures with different d-spacings were observed.
3. The amount of amorphous material increases with the addition of either EG or pBP.
4. EG and pBP may be incorporated into the CSH structure and may exist in the micropores between CSH constituents.
5. EG and pBP are observed to absorb onto some of the $Ca(OH)_2$ and $Mg(OH)_2$ crystals.
6. Small amounts of fine crystals are found in EG and pBP containing cements. Their d-spacings could be determined but did not correspond to any of the expected products of the hydration of pure

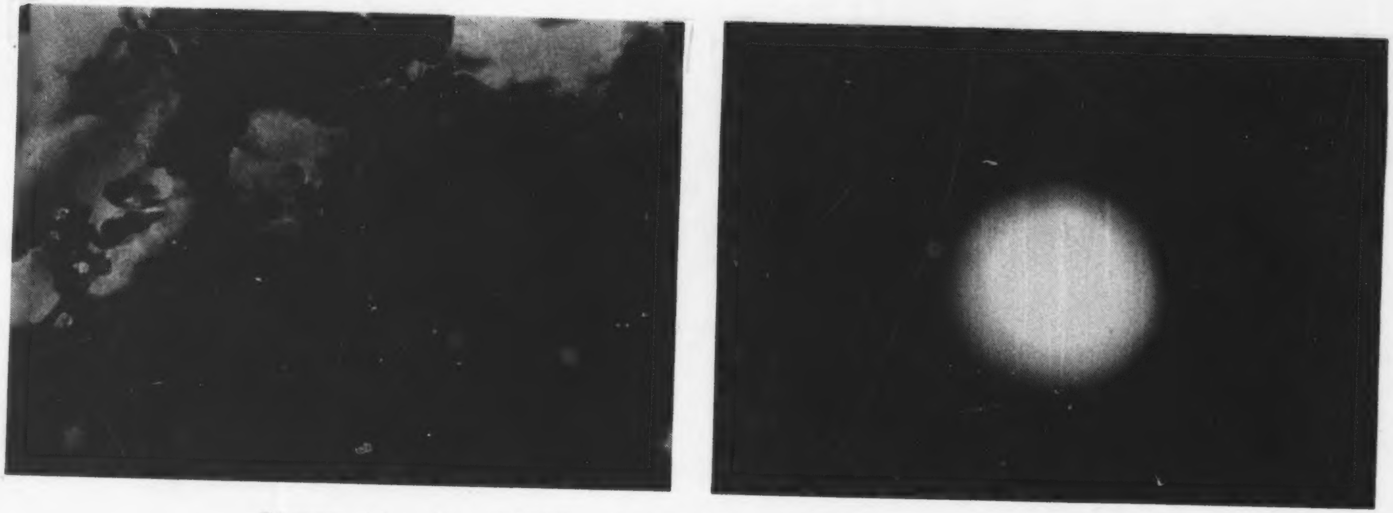


Figure 19. An unstable phase in p-promophenol-containing cement
O/C = 0.1; age = 6 months.

cement.

X-RAY DIFFRACTION OF pBP AND pCP SAMPLES

The physical properties of Portland cement are ultimately controlled by phases present in it and their microstructure. Organic compounds can strongly affect the physical properties of Portland cement by inhibiting crystallization of certain phases and modifying the microstructure. X-ray diffractometry is an excellent tool to study the changes in crystallinity and appearance or disappearance of phases. The model system chosen here involves Portland cement and pBP. Three samples were made containing 0.04 (B-25), 0.1 (B-10), and 0.2 (B-5) weight ratios of pBP to cement. The water to cement ratio was 0.4. One sample containing pCP was also studied to examine whether the similar organic compounds behaved similarly or not.

The x-ray diffraction pattern of pure Portland cement is not very well characterized. Many peaks present in the pattern cannot be assigned to a particular phase because the phases present in cement themselves are not well known. The XRD pattern furnished by Gutteridge (Cement and Concrete Association) from an Italian study[31] shows the peaks that are present in a Portland cement sample before and after removal of portlandite, $Ca(OH)_2$. A large proportion of portlandite is likely to mask other peaks. A control sample, containing no pBP, has also been characterized by XRD for the present study. From the patterns of the Italian study[31] and the control sample run here a composite pattern has been produced which should contain most of the peaks expected in hydrated Portland cement. Any changes caused in Portland cement by pBP can be characterized by comparing this composite pattern with the XRD pattern of Portland cement samples containing various quantities of pBP. The JCPDS powder data file (1984) can also be used to identify the various phases. The d spacings, corresponding to which peaks are present in the Portland cement XRD patterns of the Italian study and the samples prepared for this study are shown in Table 22.

TABLE 23

Intensities of Prominent CH and CSH Peaks

	$Ca(OH)_2$		CSH	
Sample	Peak (A)	Intensity (cps)	Peak (A)	Intensity (cps)
Control	2.617	2706	3.014	664
B-25	2.625	1453	3.025	601
B-10	2.63	1276	3.031	475
B-5	2.633	682	3.042	408

Table 22

d-spacings (angstroms) of Control and pBP Samples

Italian[31]	CONTROL	B-5*	B-10	B-25
8.90 $C_3A \cdot CaSO_4 \cdot 12H_2O$				
8.14 C_4AH_{12}				
7.75				
7.60				
5.96 $CaSO_4 \cdot \frac{1}{4}H_2O$				
5.71				
5.42				
5.23				
5.06 C_3AH_6				
4.98 $Ca(OH)_2$				5.017
		4.956	4.956	
	4.82 $Ca(OH)_2$			
		4.770+		
4.68			4.727	
4.66				
4.46 $C_3A \cdot CaSO_4 \cdot 12H_2O$				
4.45				
4.38 C_3AH_3	4.38			
4.14				
4.13				
4.10				
4.07				
4.05 C_4AH_{13}				
3.92 $C_3A \cdot CaSO_4 \cdot 12H_2O$				
		3.941		
3.85		3.862		
			3.835	
			3.739	
		3.720		
3.60		3.663+		
		3.608		
3.56			3.570	
			3.533	
		3.523		
3.37		3.374		
3.3 C_3AH_6				
		3.324		
			3.318	3.318
	3.319			
3.30				
3.29				

(Continued)

Table 22 (Continued)

d-spacings (angstroms) of Control and pBP Samples

Italian[31]	CONTROL	B-5*	B-10	B-25
			3.286	
3.20	3.259	3.252	3.262	
3.13	3.206			
		3.129		
3.07	3.088		3.108	3.105
3.03 CSH + $CaSO_4 \cdot \frac{1}{4}H_2O$		3.042		
	3.014		3.030	3.025
		2.960+	2.962	
2.94				2.953
2.87 C_4AH_{13}	2.863	2.873	2.879	2.920
2.18				2.872
2.79 C_3AH_6				
2.76 CSH + $CaSO_4 \cdot \frac{1}{4}H_2O$	2.755	2.773		2.771
2.73 C_4AH_{13}			2.763	
2.65		2.692+		2.732
		2.633	2.630	
2.60	2.617 $Ca(OH)_2$			2.625
		2.550		
2.53	2.542		2.548	2.541
2.50	2.522			
2.49				
2.45 $C_3A \cdot CaSO_4 \cdot 12H_2O$				
2.43				
2.42				
2.25				
		2.202	2.190	2.195
		2.184+		
2.16				2.179
2.14 $CaSO_4 \cdot \frac{1}{4}H_2O$				
2.09				2.102
2.08		2.097		

(Continued)

Table 22 (Continued)

d-spacings (angstroms) of Control and pBP Samples

Italian[31]	CONTROL	B-5*	B-10	B-25
2.06				
2.01 C_3AH_6		2.058	2.055	2.052
			1.987	
		1.976+	1.974	
1.93				
	1.927 $Ca(OH)_2$	1.921	1.927	1.928
		1.902+	1.904	
1.88				
1.87 $Ca(OH)_2$		1.874		
1.85			1.851	
1.83 $CaSO_4 \cdot \frac{1}{4}H_2O$	1.829	1.830		
			1.823	1.829
1.81 $Ca(OH)_2$ (?)		1.814		
	1.796 $Ca(OH)_2$	1.790	1.795	1.795
		1.759	1.765	1.765
	1.688 $Ca(OH)_2$	1.681	1.686	1.688
	1.660 Etrngte	1.664	1.662	
	1.487 $Ca(OH)_2$	1.481	1.484	1.486
	1.459			
	1.317 $Ca(OH)_2$			
	1.228			
	1.216 $Ca(OH)_2$	1.213		1.218

* - p-Bromophenol containing samples. B-5, B-10, and B-25 refer to samples containing 1:5, 1:10 and 1:25 weight ratios of pBP to cement.

+ - These are the peaks not present in either the Italian sample or in the LSU control sample. They are presumably due to any new phases that are forming.

The crystallinity of Portland cement is visibly affected by pBP. The intensities corresponding to $Ca(OH)_2$ and CSH peaks are shown in Table 23 for four different samples containing none or gradually increasing amounts of pBP. All the patterns have been acquired under identical conditions. The intensity of the 2.63 A $Ca(OH)_2$ peak has been reduced by a factor of two in B-25 and by a factor of four in B-5 compared to the control sample containing no organics. The CSH peak is similarly affected, but the reduction in intensity is less drastic. Addition of the organic has presumably led to crystallization of less $Ca(OH)_2$ and CSH. The reduction in intensities may also be explained by reduction in grain size.

The total number of peaks in the composite patterns is much higher than in pBP-containing samples. Fewer peaks in pBP-containing samples may be due to various reasons: a) lower crystallinity in the above samples may have led to the disappearance of weaker peaks; b) the XRD runs of the Italian study may have been performed at slower speed so that the peaks were better resolved; c) pBP may have inhibited crystallization of certain phases; d) other phases, e.g. $Ca(OH)_2$, may have masked some peaks.

Though pBP-containing samples have fewer peaks than the composite pattern, some peaks present in the former group are absent in the composite pattern (marked by +). The composite pattern is likely to contain all the peaks due to the phases in pure Portland cement. The unmatched peaks in pBP samples are then due to a new phase(s), presumably formed by reaction of the organic compound with Portland cement.

Chemically the bulk of Portland cement is calcium. A new phase produced by reaction of pBP with Portland cement is mostly likely to be composed of calcium and bromine. That the new peaks pBP-containing samples are indeed due to such a compound was verified by preparing a calcium salt of pBP, and then analyzing it by XRD. The pattern is shown in Fig. 20, along with those for a cement control, 1:25 pBP and 1:5 pBP in Figs. 21-23. The peaks from Fig. 20 are listed in Table 24. The low intensity of the peaks suggest poor crysallinity. Some of the d spacings of this compound can be matched with the peaks in pBP-containing cement samples. Unfortunately, the most intense peak of the calcium salt of pBP is covered by a $Ca(OH)_2$ peak. Thus it is likely that the new phase is a calcium salt of pBP, but it cannot be conclusively shown. However, as Portland cement contains many other elements, e.g., Al, Fe, etc., they may also enter the new phase. The XRD pattern of such a compound may be little different from that of a simpler calcium salt of pBP.

The results of the above study can be summarized as follows. pBP affects the crystallinity of Portland cement. Interaction of pBP with Portland cement leads to formation of new phases as seen by the appearance of new peaks in the XRD patterns. These new phases are complex solid solutions of different elements, but mostly composed of calcium and bromine.

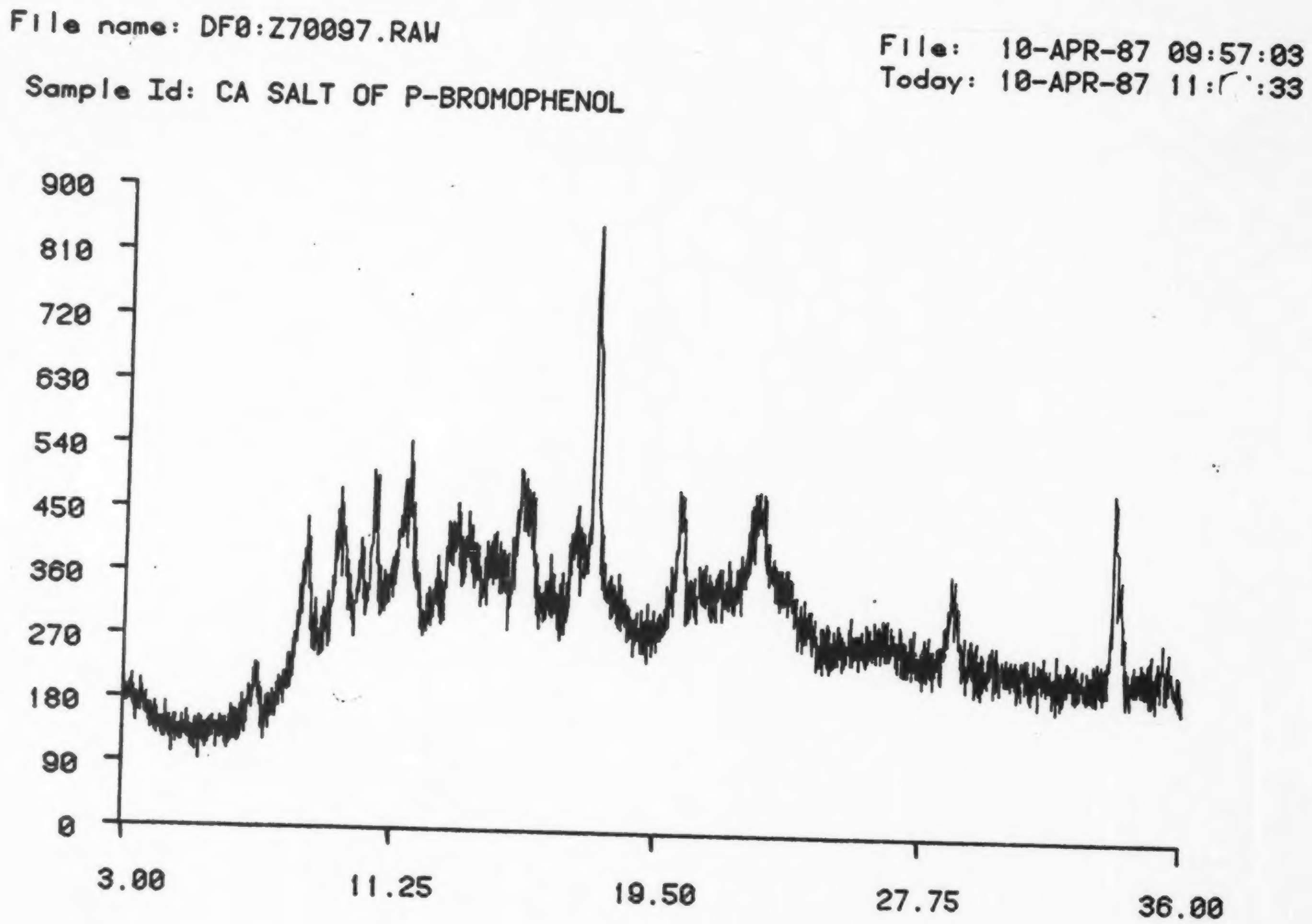


Figure 20: XRD pattern of Ca salt of p-bromophenol.

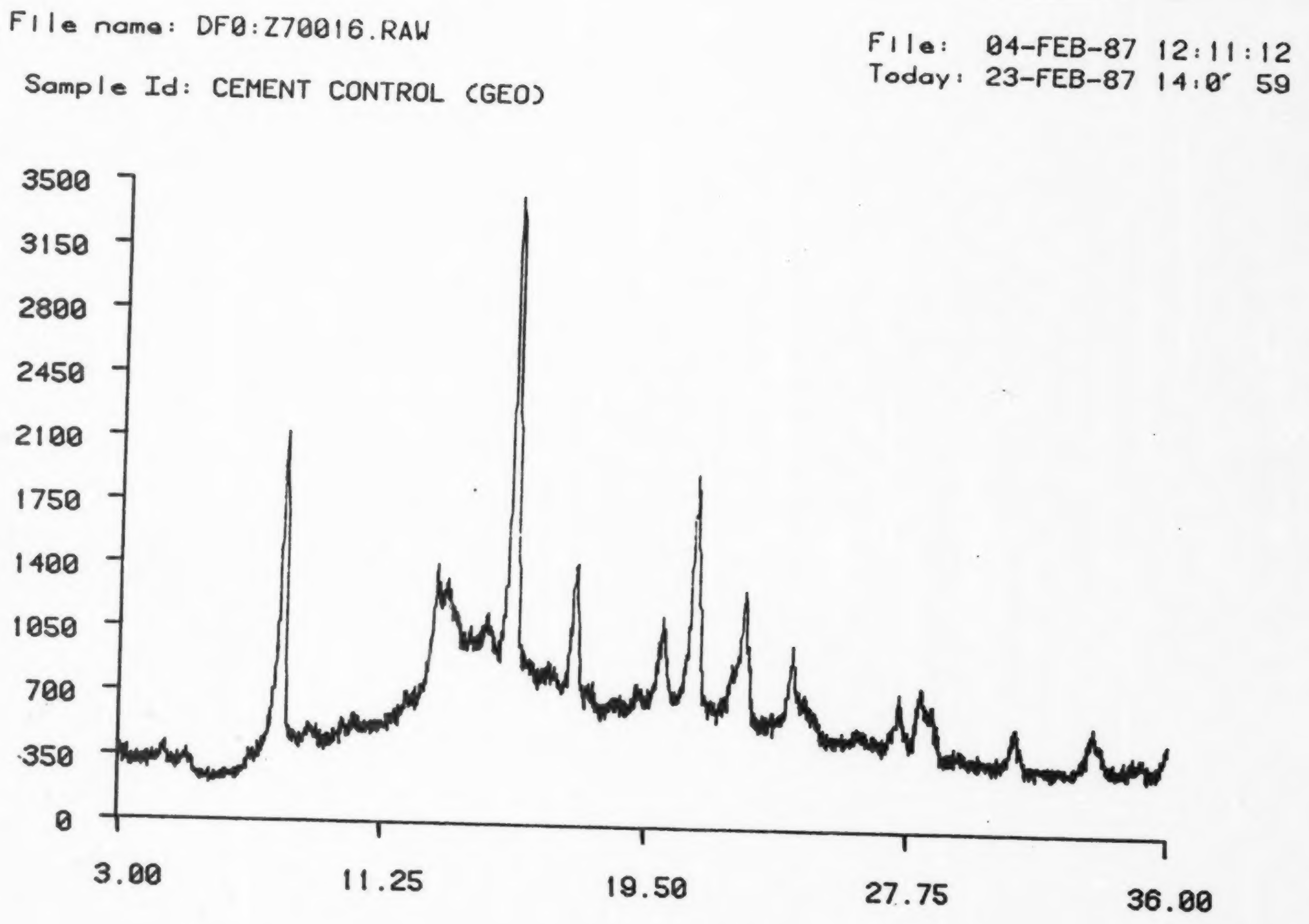


Figure 21: XRD pattern of cement.

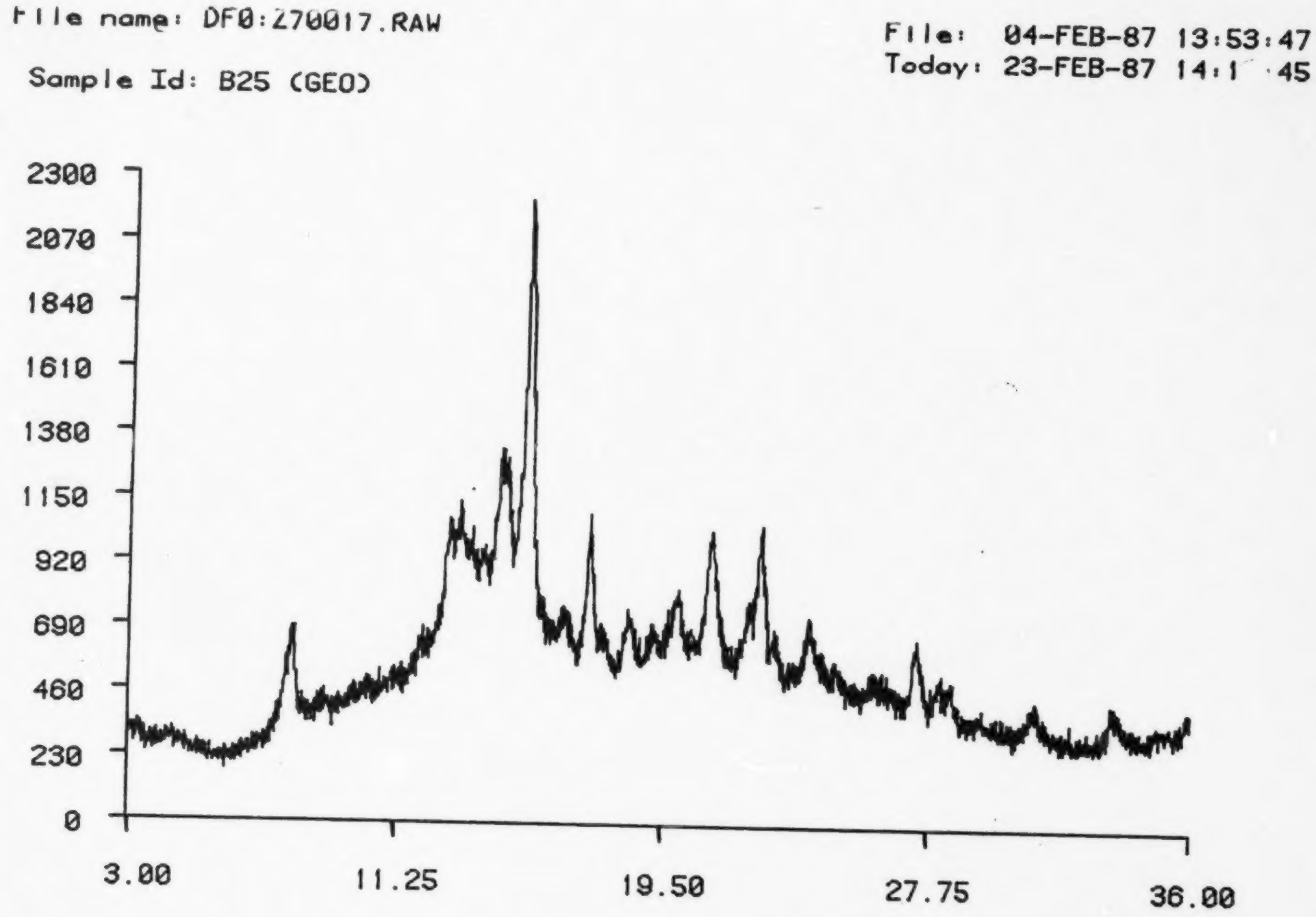


Figure 22: XRD pattern of 1:25 pBP/cement.

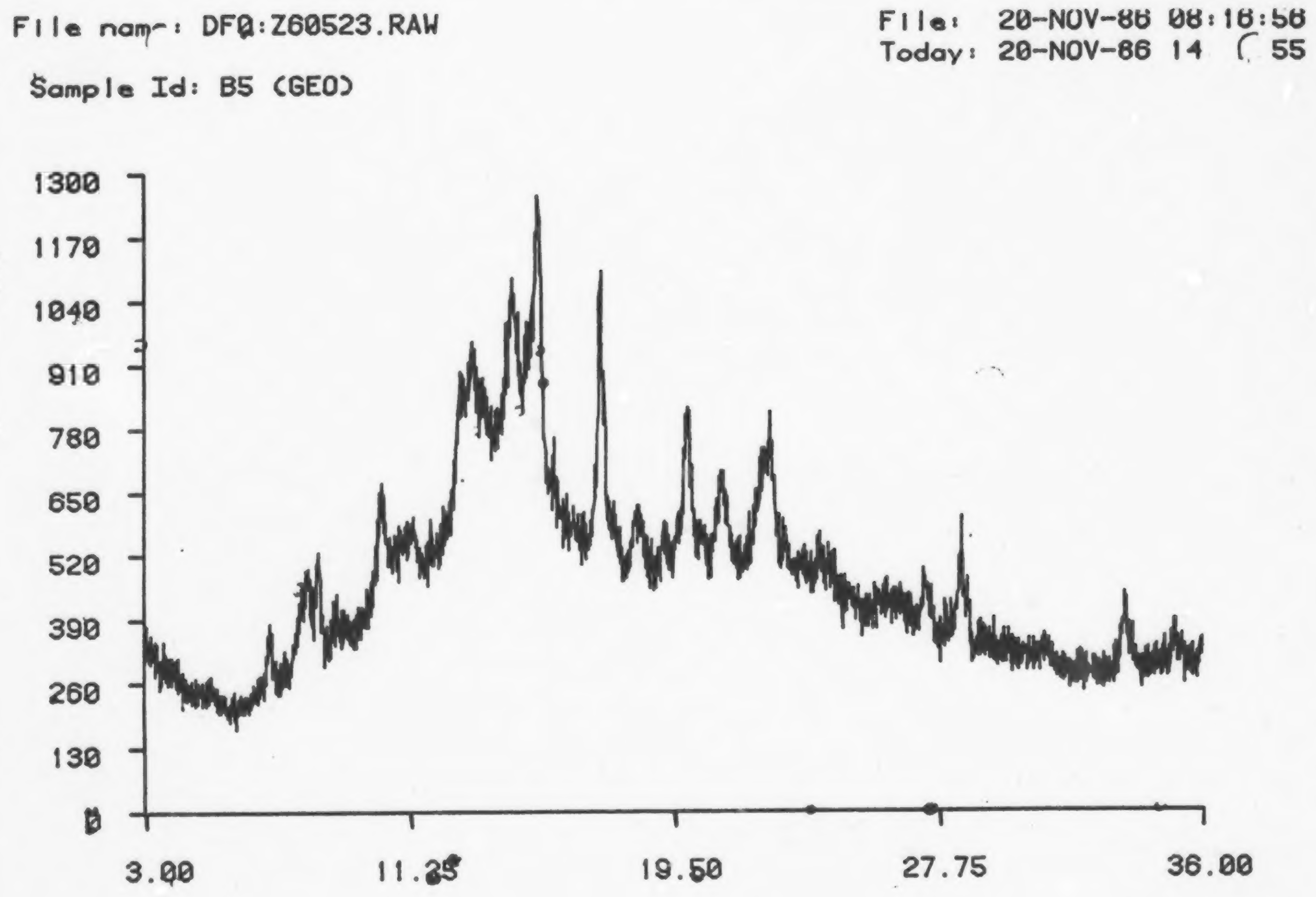


Figure 23: XRD pattern of 1:5 pBP/cement.

TABLE 24. d-Spacings of Calcium p-Bromophenoxide and in B-5.

Ca salt of p-Bromophenol		
d-spacing (Å)	Int. (cps)	Unmatched peaks in B-5 d-spacing (Å)
4.930	40	
4.362	76	4.770
3.921	88	
3.789	32	
3.622	69	3.663
3.532	95	
3.455	17	
3.186	43	
3.121	63	
3.042	42	
2.979	24	
2.708	58	2.960
2.649	24	2.692
		2.184
1.965	29	1.976
1.950	33	
1.927	0	
1.909	32	
1.891	16	1.902
1.878	16	
1.852	36	
1.826	54	
1.808	93	
1.794	100	
1.769	54	
1.743	32	1.759
1.729	43	

The d-spacings corresponding to the peaks present in the XRD pattern of the calcium salt of p-bromophenol are shown in the left column. The d-spacings in B-5, which could not be matched with the composite pattern of pure Portland cement are shown under B-5.

PHYSICAL PROPERTIES OF EG, pBP AND pCP SAMPLES

Setting time

Table 25 lists the initial and final setting times for the various ratios of organic compounds and cement. These values are illustrated in Figure 24. The control sample has an initial setting time of 255 minutes and final setting time of 295 minutes. Ethylene glycol (EG) has a significant effect on setting at all concentrations. p-Chlorophenol (pCP) at moderate and high concentrations increased setting time. p-Bromophenol (pBP) at moderate and high concentrations slightly increased setting time.

TABLE 25
Initial and Final Setting Times for Type I Portland Cement Containing Various Ratios of Organic Compounds

Sample	Initial Setting Time (minutes)	Final Setting Time (minutes)
Control	255	295
EG 1:25	435	555
EG 1:10	960	1020
EG 1:5	>1440	>1440
pCP 1:25	245	325
pCP 1:10	540	650
pCP 1:5	430	515
pBP 1:25	220	290
pBP 1:10	310	445
pBP 1:5	460	500

Compressive strength

Table 26 lists the unconfined compressive strength values for the various organic/cement ratios. This data is shown in Figures 25-27. Compressive strength in the control samples significantly increased in the first seven days, leveling off to the 28 day value

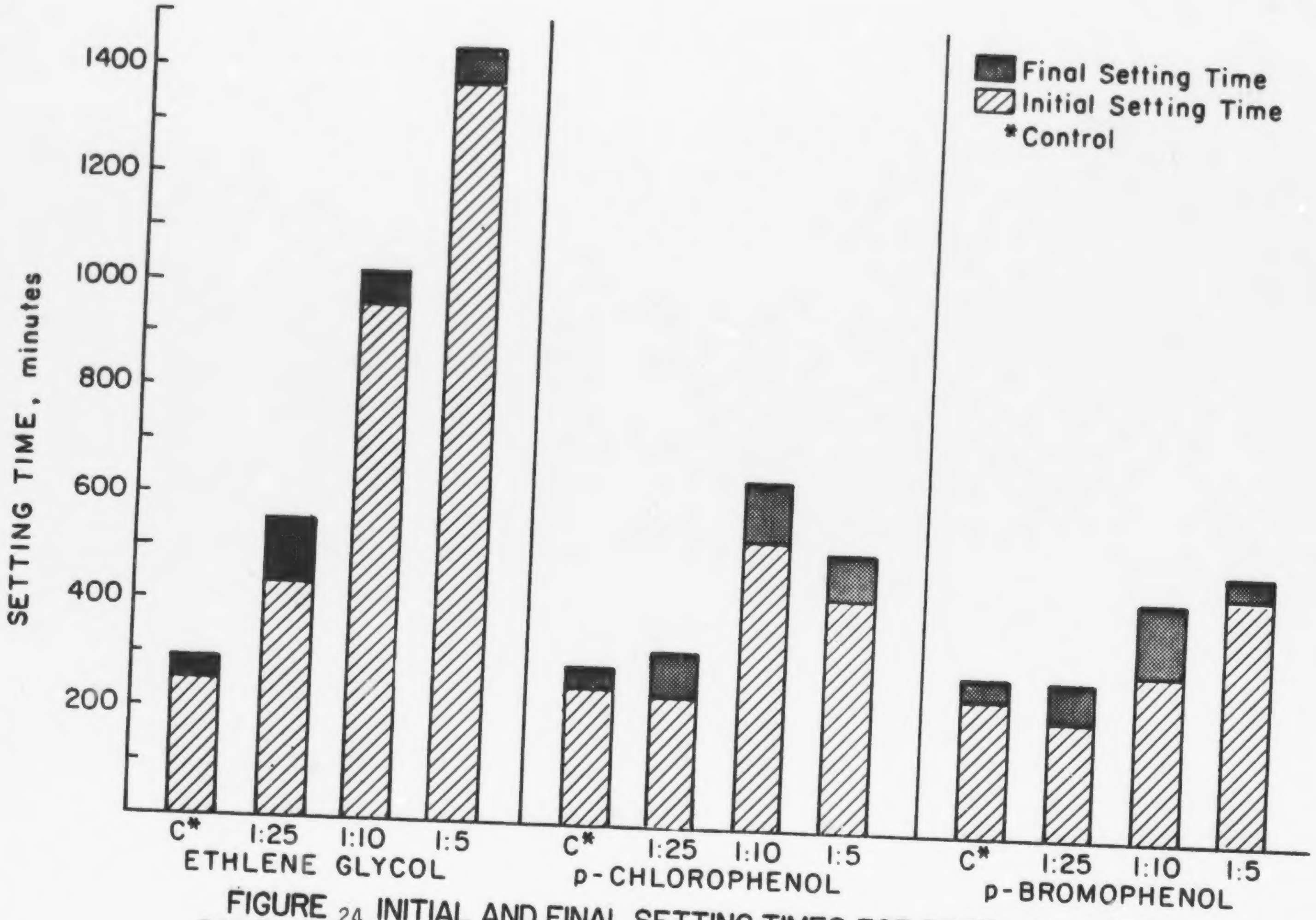


FIGURE 24 INITIAL AND FINAL SETTING TIMES FOR PORTLAND CEMENT CONTAINING VARIOUS RATIOS OF ORGANIC COMPOUNDS (0.4 W/C RATIO)

TABLE 26

Compressive Strength versus Time for Type I Portland Cement Containing Various Organic Compounds

Sample	12 Hours (psi)	1 Day (psi)	7 Days (psi)	28 Days (psi)
Control	512	1985	5981	6483
EG 1:25	53	1575	5183	6308
EG 1:10	13	83	3031	4954
EG 1:5	0	37	35	55
pCP 1:25	387	958	4971	6531
pCP 1:10	50	705	4402	6633
pCP 1:5	0	45	3125	4513
pBP 1:25	938	1039	2800	6504
pBP 1:10	353	928	3463	5708
pBP 1:5	54	470	4552	5433

of approximately 6500 PSI. EG at the low concentration had little effect on this strength pattern. For EG 1:10 samples, strength was lower compared to the control sample, but with substantial gain through 28 days. The EG 1:5 samples showed virtually no strength.

Examination by SEM and TEM shows major changes in the morphologies of the CSH phase in the presence of EG changes in the morphologies of the CSH phase in the presence of EG. It is the tobermorictic material which is considered primarily responsible for strength[5]. Overall crystallinity was also observed by XRD and SEM to diminish with increased EG concentrtion[27]. However, while the high concentration of EG had virtually no strength, samples with low and moderate EG concentrations did show some strength. This occurrence may be related to the degree of porosity in the samples. SEM micrographs have shown high concentration EG samples to be very porous, while the low and moderate EG concentrations basically resembled the porosity of the control samples[27]. The morphological changes and diminished crystallinity in the EG samples were greatly accentuated in the EG 1:5 as compared to the 1:10 ratio (see preceding discussion of SEM). This could explain the large drop-off in strength from the 1:10 to the 1:5 ratios. Therefore, the adsorption onto C_3A and CH probably delays the development of crystalline structure at low concentrations of EG, while at high concentrations formation of crystalline structure is effectively blocked.

TABLE 27

Percent Recovery of Organic Compounds versus Time

Sample	12 Hours (psi)	1 Day (psi)	7 Days (psi)	28 Days (psi)
EG 1:25	100.0	96.8	89.6	84.9
EG 1:10	95.5	97.8	88.5	79.6
EG 1:5	100.0	95.8	95.4	93.8
pCP 1:25	77.1	73.6	73.9	73.4
pCP 1:10	89.0	88.3	85.9	78.3
pCP 1:5	94.6	89.0	61.5	53.0
pBP 1:25	73.8	65.9	44.6	41.0
pBP 1:10	93.1	89.8	48.0	42.0
pBP 1:5	100.0	95.9	48.2	47.0

pCP samples had higher compressive strength than EG samples. At low and moderate pCP concentrations, the compressive strength values were less than the control samples through 7 days. However, both the 1:25 and 1:10 ratios reached the strength level of the control sample at 28 days. This increase is probably due to a delayed formation of CSH gel. Examination by SEM has shown 12 hour pCP samples at low and moderate concentrations to have larger pores than 12 hour control samples. However, at 28 days these samples seemed relatively non-porous. The gain in strength is presumably due to an increase in hydration products at later times, but the hydration products are much less crystalline in the presence of pBP. With time, as strength develops, the silicate structures undergo polymerzation from simple SiO_4 structures to Si_2O_7 to polysilicates[39]. Whether this process is interferred with by pCP is not known.

pBP samples at all concentrations gained substantial strength through 28 days. At the low and moderate concentrations, gain was more appreciable from 7 to 28 days, whereas the high concentration had significant gain between 1 day and 7 days.

pBP samples had compressive strength values higher than EG samples, and comparable with pCP samples. Interestingly, pBP 1:5 reached a higher 7 day strength than the low or moderate pBP concentrations. Many spiney or needle-like features have been found by SEM to be more predominant in the higher concentration pBP than in lower pBP concentrations or in control samples[40]. Possibly these needle-like features contributed to the early strength of the pBP 1:5 samples. Needle-like morphology is a characteristic of CSH. A disproportionate amount of strength has been suggested to result from the interlocking of fibrillar crystalls that occur during the outward growth of CSH[41]. At 28 days, the pBP 1:25 samples had the highest compressive strength, reaching the level of strength developed by the control sample. SEM images of pBP 1:25 samples have exhibited massive, dense surfaces, similar to 28 day control samples[40]. Like pCP samples, the crystalline hydration products continue development after initial delay, resulting in a rebound up to the strength level of the control sample.

Leachability

Table 27 lists the percent recoveries for the organic compounds. Figures 28-30 show the data graphically.

EG samples had very high recovery rates when extracted by water (>80 percent). Once again, the greater porosity exhibited by SEM is one reason for the high rate of recovery. The higher porosity results in more EG being available for leaching because EG is thought to exist in the micropores between CSH constituents[42]. Also, EG is very soluble in water, so it can be readily removed from the surfaces of the hydrated cement particles by an aqueous solution.

pCP had lower percent recoveries than EG, but all of the values were above 50%. EPMA has shown that pCP was found almost uniformly dispersed in the CSH gel phase, but not entered in the cement grains nor coated around the cement grains as pBP did. But because the pCP molecule is much larger than the EG molecule, the pCP may be more difficult to remove through the pore spaces. pCP is also less soluble in water than EG, so it may be more difficult to remove from the surfaces of cement particles.

pBP had the lowest recoveries of the three organic compounds utilized. There was a definite trend of a significant decrease in recovery between 1 day and 7 days. Here the recovery reached a plateau at less than 50%. Possibly a large portion of the pBP not recovered is the approximate 43% that forms its own unique phase. EPMA examination has shown the phase to be a reaction with cement components that form a concentrated, very localized phase, which is distributed as both equiaxed and irregular shaped grains[36]. pBP is less soluble in water than pCP, and pBP is larger than pCP, so it is more resistant to leaching.

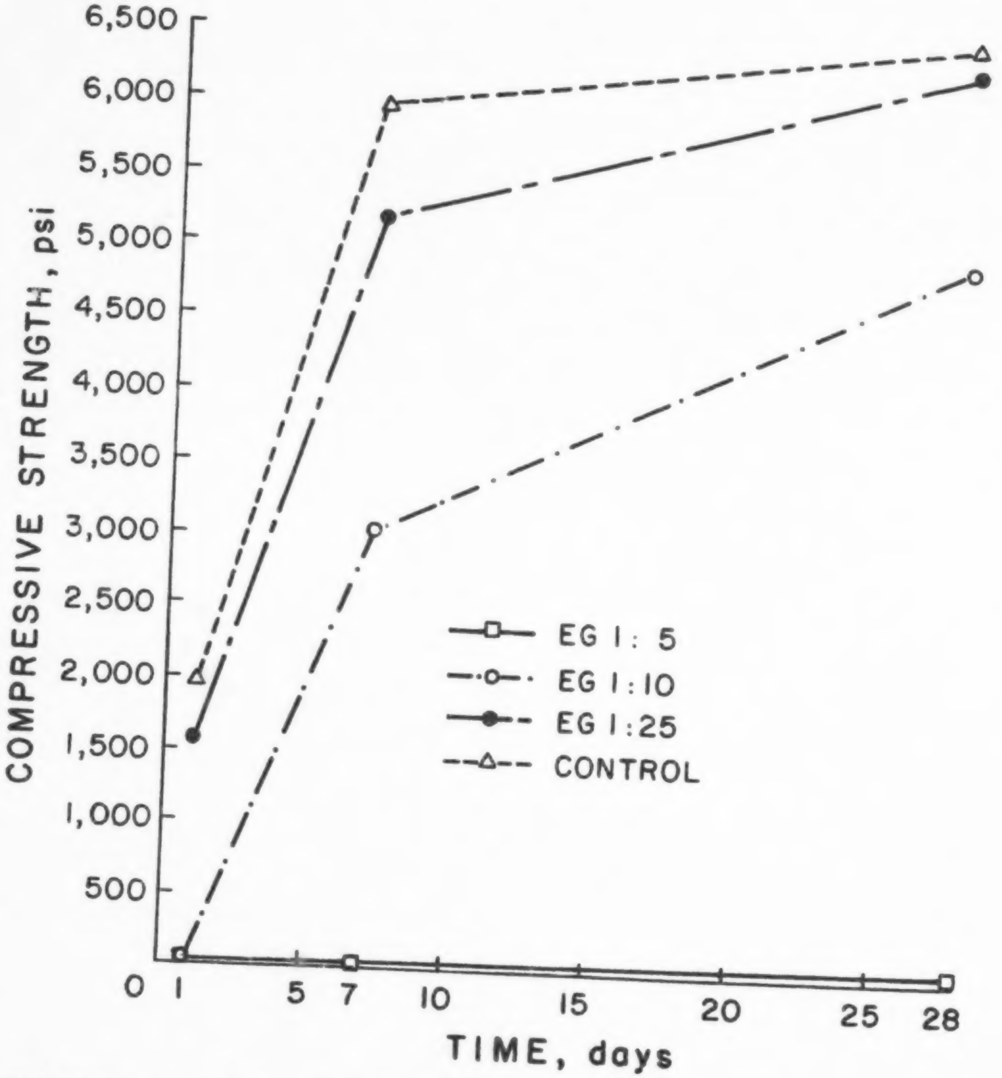


FIGURE 25 COMPRESSIVE STRENGTH OF PORTLAND CEMENT CONTAINING VARIOUS RATIOS OF ETHYLENE GLYCOL (0.4 w/c ratio)

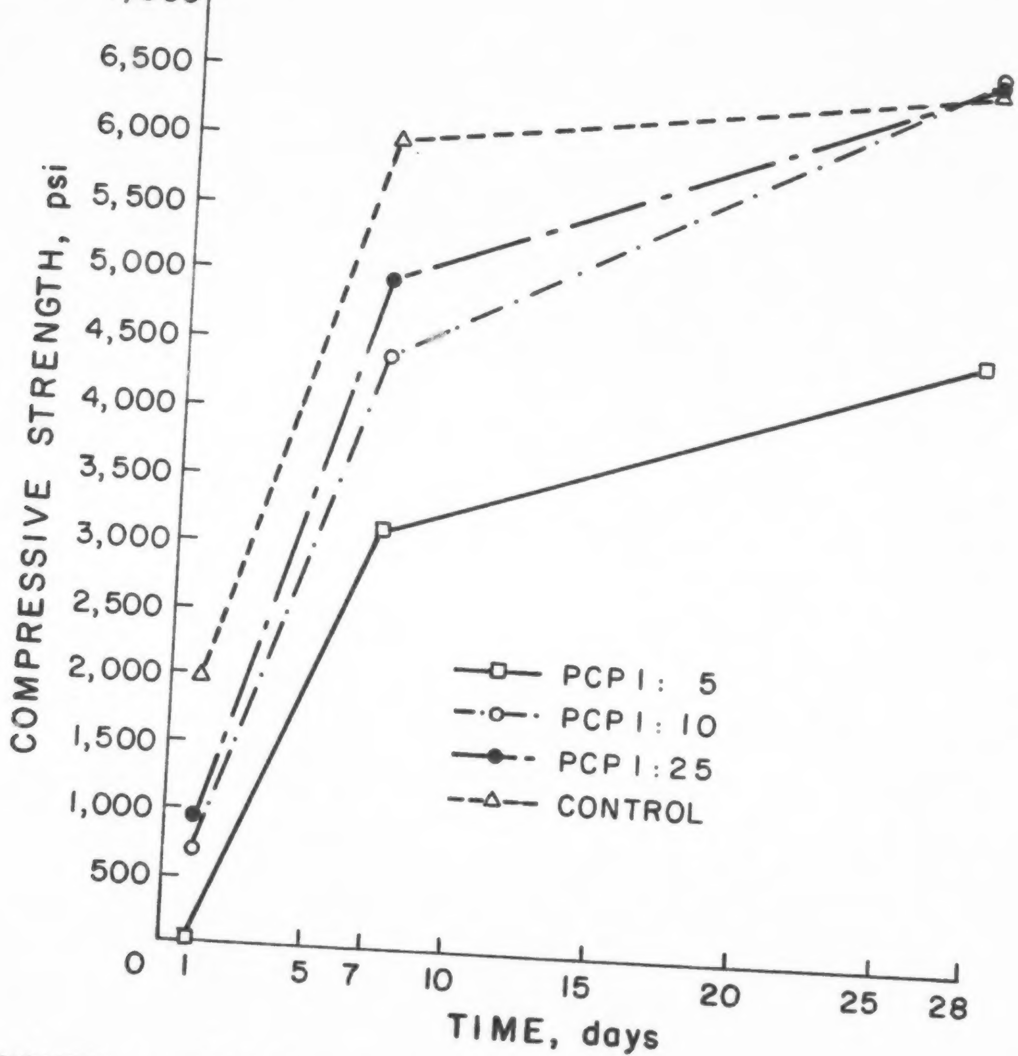


FIGURE 26 COMPRESSIVE STRENGTH OF PORTLAND CEMENT CONTAINING VARIOUS RATIOS OF P-CHLOROPHENOL (0.4 w/c ratio)

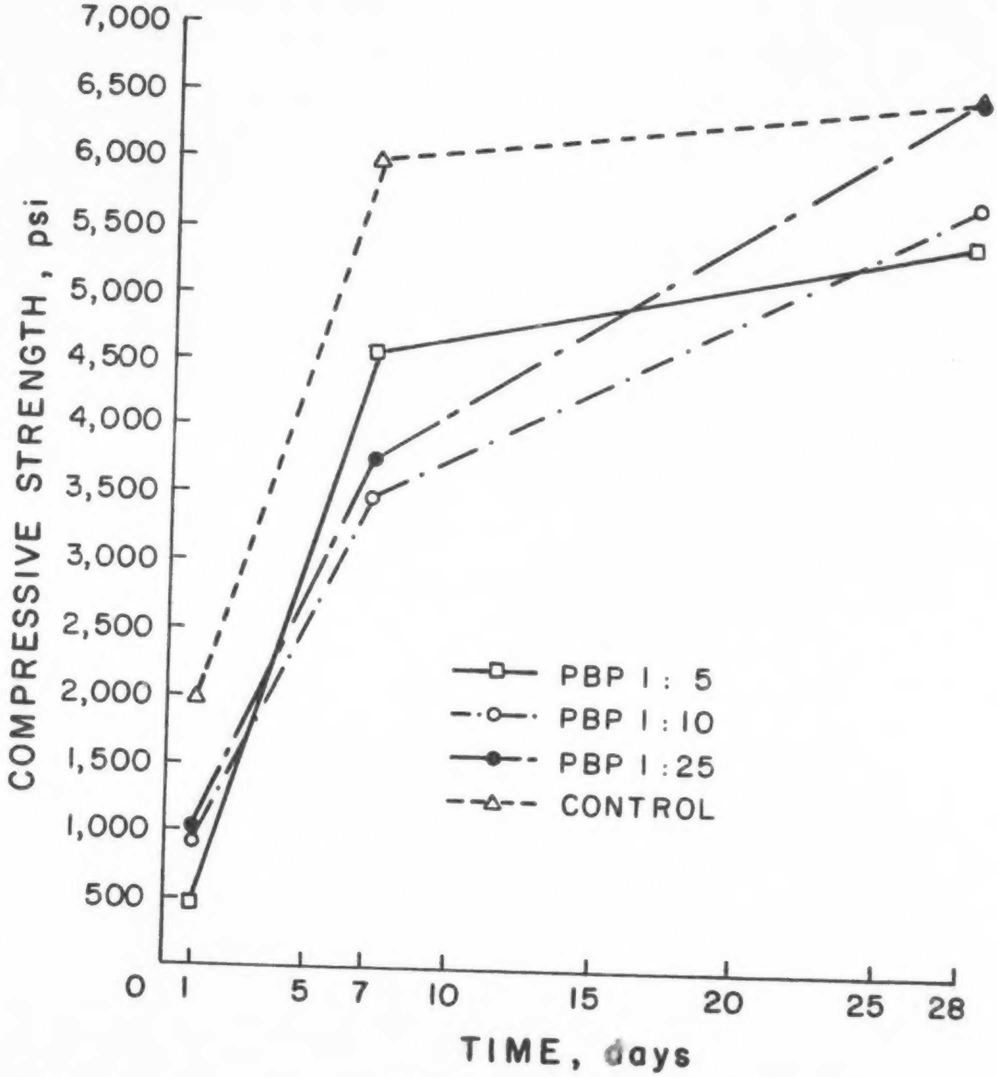


FIGURE 27 COMPRESSIVE STRENGTH OF PORTLAND CEMENT CONTAINING VARIOUS RATIOS OF P-BROMOPHENOL (0.4 w/c ratio)

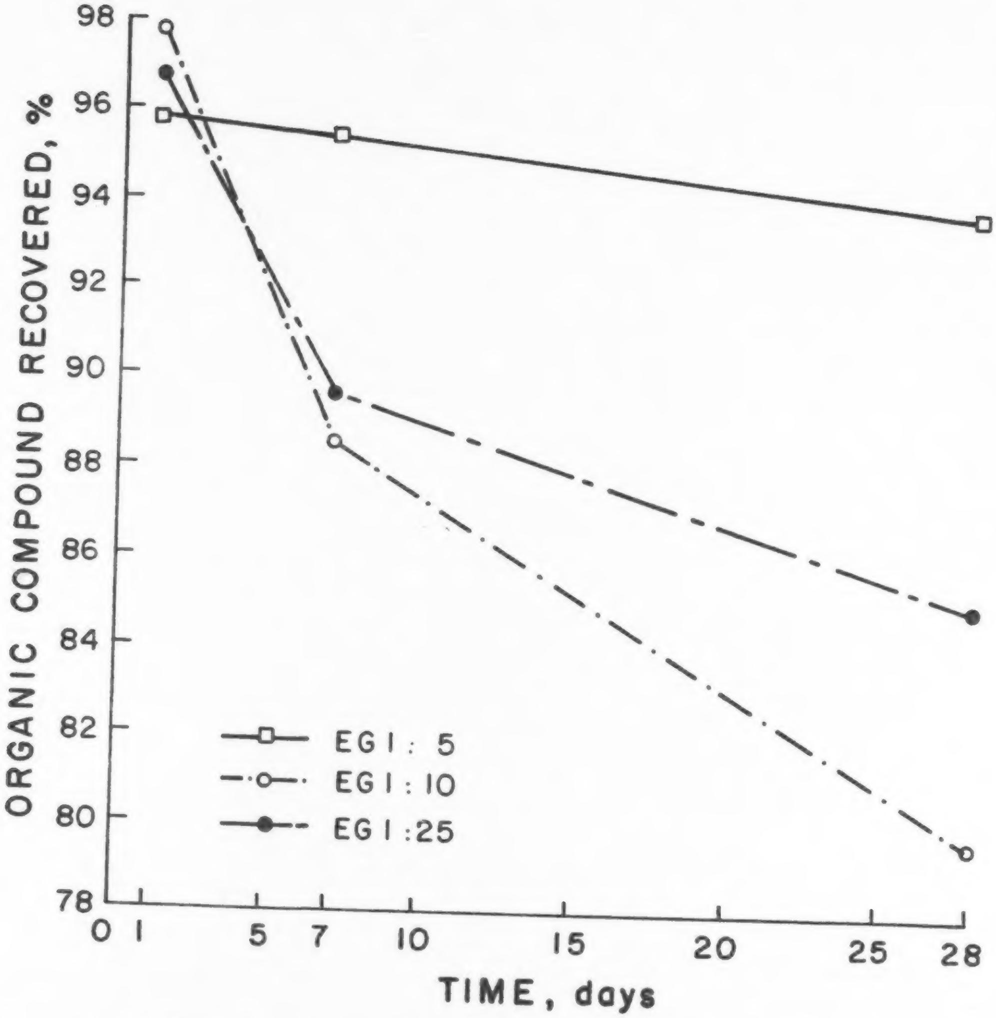


FIGURE 28 PERCENT RECOVERY OF ETHYLENE GLYCOL FROM E.P. TOXICITY TEST (0.4 w/c ratio)

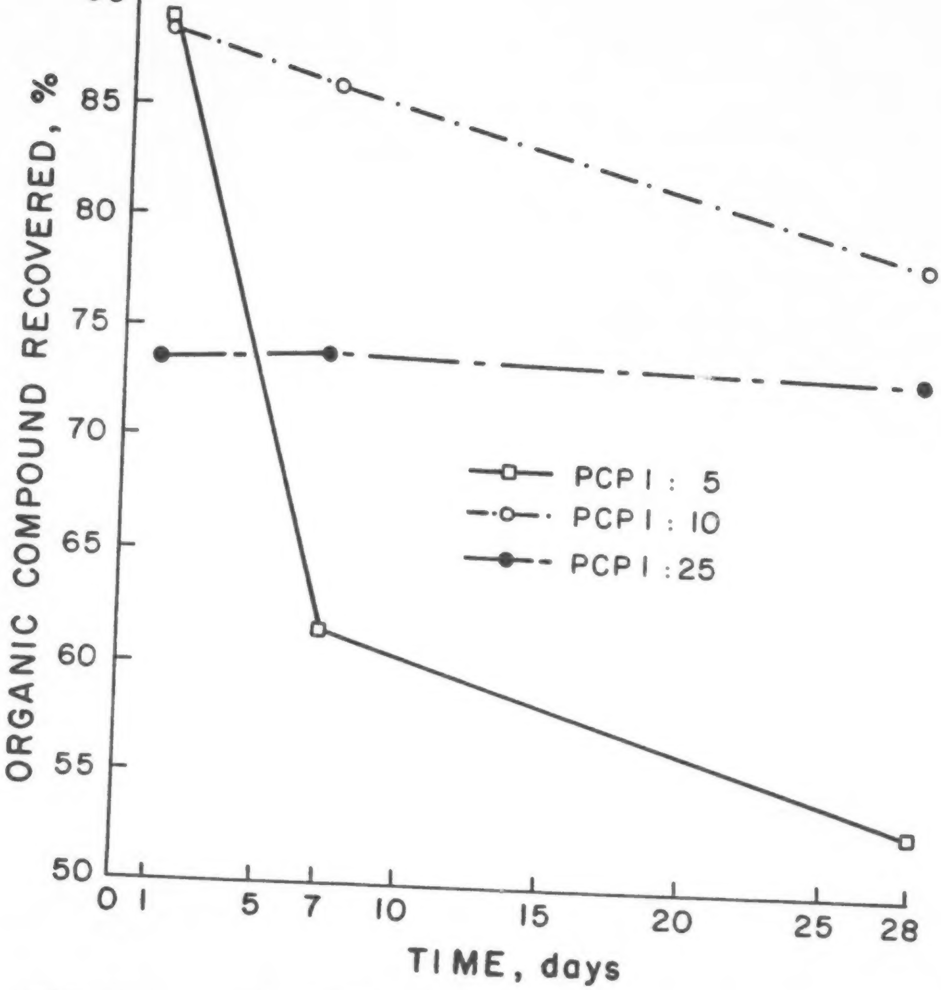


FIGURE 29 PERCENT RECOVERY OF P-CHLOROPHENOL FROM E.P. TOXICITY TEST (0.4 w/c ratio)

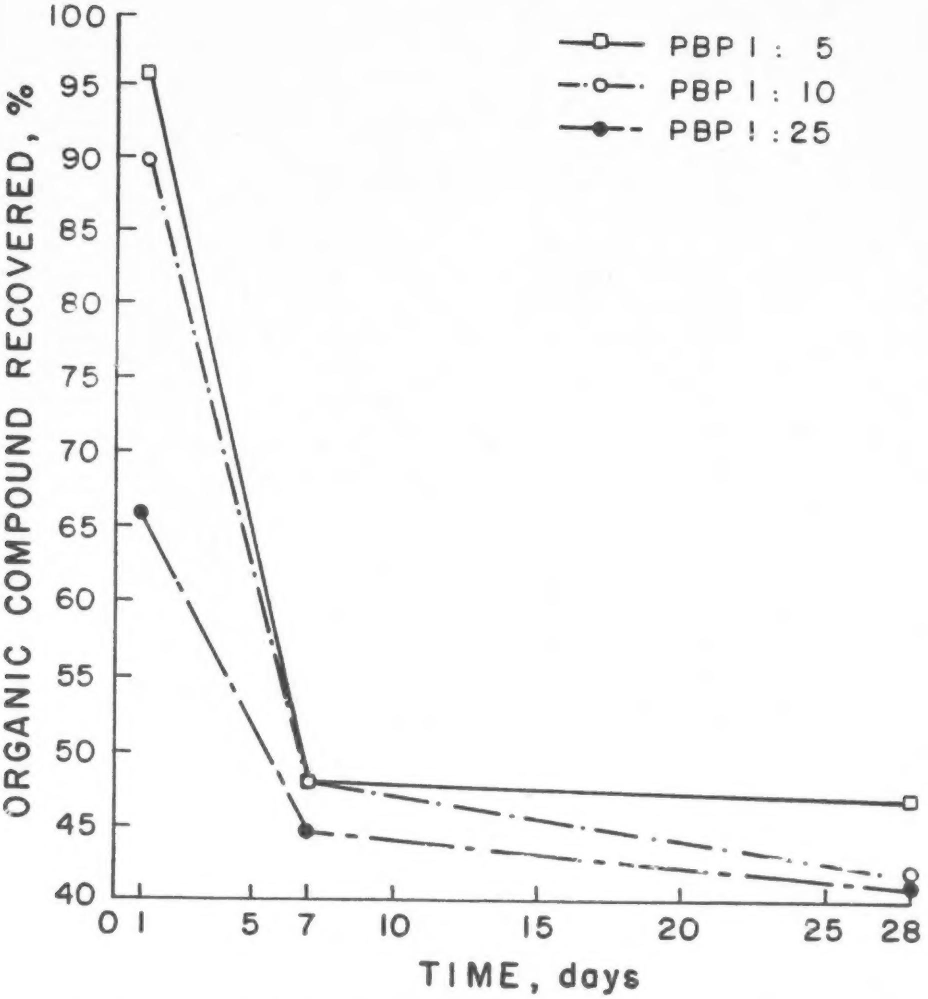


FIGURE 30 PERCENT RECOVERY OF P-BROMOPHENOL FROM E. P. TOXICITY TEST (0.4 w/c ratio)

Discussion of physical tests

The hydration of Portland cement may be thought of as a complex dissolution-precipitation process in which the various hydration reactions proceed simultaneously at differing rates and influence each other[32]. This process consists of three distinct but over-lapping phases: a dispersion or "colloidization" of cement particles (primarily C_3A - tricalcium aluminate), followed by the formation of a coagulated thixotrophic structure from the dispersion of unhydrated cement components and hydration products (setting), and development of a crystalline structure by precipitation from a super-saturated solution (hardening)[32]. The main hydration products of Type I Portland cement are calcium silicate hydrates (CSH) and calcium hydroxide (CH), which form from tricalcium silicate (C_3S) and dicalcium silicate (C_2S).

Addition of EG greatly increased the setting time of the cement. TEM (transmission electron microscopy) tests have shown EG to form small cubic crystals thought to be a new phase incorporating EG and C_3A[33]. It is known that most abnormal setting can be traced to chemical reactions involving the aluminates such as C_3A in the early hydration period[5]. There is good reason to believe that adsorption through hydrogen bonding occurs on C_3A. A common form of hydrogen bonding is attachment of hydroxyl groups to oxygen atoms, and all of the major clinker compounds are combinations of oxides[34]. Ethylene glycol has two hydroxyl groups, so its adsorption on cement clinker compounds is pronounced. Organic retarders can influence the rate of formation of the coagulated structure of cement along with the speed and form of the crystallization of the aluminate hydration products[35]. EG also has been shown to adversely affect hydration of C_3S. TEM studies have shown EG to be combined with CH crystals[33]. An earlier study suggests the formation of CSH is caused by the deposition of silicate anions on the surface of a preformed CH lattice acting as a nucleant[36]. Through organic adsorption onto CH nuclei, CSH formation would be retarded[37]. Therefore, EG delays formation of all main hydration products.

pCP also increased the setting time of cement samples, although not as much as EG. At the low pCP concentration, the initial setting time was lower than that of the control, while the final setting time was greater than that of the control. It has been shown that small dosages of an organic retarder can actually accelerate the initial hydration of a cement paste before retardation begins[37]. SEM/EDAX has shown pCP to be found almost uniformly in the CSH gel phase, as described earlier in this report. So, like EG, pCP likely slows the hydration rate of C_3A. pCP also is believed to be adsorbed through hydrogen bonding onto C_3A. pCP has one hydroxyl group on its phenolic ring. EDAX tests, at 143 random points in an area of pCP/CSH formations, showed samples contained a greater percentage of aluminum than calculated for the sample as a whole, which indicates adsorption of pCP by the C_3A (see earlier discussion).

pBP had the least effect on the setting of cement samples. EPMA (electron probe microanalysis) has shown that pBP is found principally in a Br-rich phase rather than distributed uniformly in the CSH phase[38]. It appears to do little to hamper the process of Portland cement setting.

pBP has also been shown by EPMA to be heterogeneously distributed in the cement matrix or coated around cement grains[38]. SEM studies have shown the pBP rich areas to have only minor amounts of Al and Si present. The waste phase is essentially Br and Ca and is thought to be the calcium salt of pBP (see preceding discussion of XRD). pBP may retard partially through interfering with CH and the subsequent formation of CSH gel as EG does. Other cement grains were shown by EPMA to be clear in the center but had a Br rich outer rim[38]. Through adsorption of an organic, cement particles can acquire a negative potential. This potential will orient the water dipoles around each cement particle and form a hydrated sheath which acts mechanically to prevent close approach between the cement particles, retarding the set[34]. Therefore, pBP probably surrounds some cement particles, delaying their ability to aggregated.

CONCLUSIONS

The systems studied in the present work now represent the most thoroughly characterized combinations of organics with cement pastes. In particular, the cases studied include relatively high concentrations of organics, which would be typical of situations in which organics would constitute a large fraction of a waste mixture which was being colidified. Two aspects of the present study with organics are particularly relevant to solidification practice; namely, the ability of cementitious matrices to immobilize the organics themselves and the effects of the organics in altering the cement matrix and thus affecting immobilization of inorganic constituents. The present study in its current state has effectively demonstrated that cement alone is ineffective in immobilizing water-soluble organics such as ethylene glycol (EG) or phenols. The second question is not completely answered to date. Many effects of the organics on the cement matrix at various concentrations have been documented. However, the leaching studies required to determine whether the organics constitute interferences in inorganic immobilization remain to be carried out or interpreted. Some of those leaching studies have been carried out as part of the Waterways Experiment Station project referred to in the introduction to this report and will be analyzed in our report on Phase 2 of this project. Further leaching studies of combinations of inorganic sludges and EG, pBP and pCP after solidification with Type I Portland cement are being carried out in a continuation of this research and will be reported at a later date.

The succeeding paragraphs will summarize the information obtained thus far with respect to the three systems studied in detail: EG/cement, pBP/cement and pCP/cement. In ongoing work we are trying to directly tie the observed differences due to the presence of organics to performance in immobilization. The next step after that will be to attempt to remediate some of the deficiencies of cement fixation matrices by appropriate additions to correct for the effects of the organics. The latter is a completely empirical exercise at present, but some of the information gained in this work should help to transform fixation agent formulation from an art to a science.

EG/CEMENT

A brief summary of what is known about these systems is outlined below.

1. The same basic reaction chemistry goes on during cement hydration in the presence or absence of EG, up to 1:5 EG/cement. SEM/EDX analysis is able to identify phases apparently identical to those in hydrated cement alone (although not necessarily in the same proportions as in cement alone). At concentrations of 1:5 and greater, the samples do not effectively set even at 28 days or longer.

2. EG slows the rate of hydration of cement, even in the 1:50 mixtures. At 1:5 ratios final set is not reached.

3. There is a small percentage of strongly bound (although mostly reversibly bound) EG. Solvents in which EG is very soluble (DCM and DMSO), and which penetrate the cement matrix very effectively under our extraction conditions, do not always give high recoveries of EG.

4. Despite the statements in the preceeding paragraph, EG is not effectively immobilized toward water leaching even at low loadings of EG on cement. High percentage recoveries (up to 100% in a single extraction after grinding) are observed at all loadings of EG on cement at all time of cure.

5. The principal effect of EG on the microstructure of cement involves the CSH gel phase. There are noticeable effects on the morphology of this phase, particularly the presence of aggregates of small grains. EG also appears to absorb to the surfaces of $Ca(OH)_2$ crystals. Fine crystals with d-spacings uncharacteristic of common cement phases could be observed by TEM but not identified.

6. Overall crystallinity of the matrix is diminished with increasing EG concentration, particularly above about 10% EG by weight.

7. Below 1:10 EG/cement, 28 day compressive strengths are comparable to those of cement pastes alone, but above 1:10 there are significant decreases in strength.

8. Increasing EG concentration increases porosity of the matrix, as judged qualitatively by SEM.

pCP/CEMENT

1. Unconfined compressive strength is lower than for the control at 7 days but approximately equal at 28 days.

2. Times for initial and final set are approximately doubled. pCP slows the hydration of cement more than pBP but less than EG.

3. In 1:10 pCP:cement samples, % recovery in water extraction decreases with time of cure from 93% (12 H) to 60% (90 d). There is no effective immobilization at any concentration or time of cure.

4. SEM shows significant morphological differences compared to cement pastes - more porous at 12 and 24 h but less porous at 7 and 28 days.

5. EDX shows homogeneous distribution of Cl at the 10 um level. pCP is not found in the calcium hydroxide phase, and it is not found in a separate phase as pBP is.

6. XRD shows new peaks, which are probably the Ca salt of pCP.

7. XRD shows significantly decreased crystallinity.

8. Despite the observations above, pCP also allows the basic reaction chemistry of setting cement to proceed, as shown by the presence of the normal cement mineral phases.

pBP/CEMENT

1. Unconfined compressive strength is lower than the control at 7 days but approximately equal at 28 days.

2. Time for initial set is increased approximately 20%; time for final set is increased approximately 75%.

3. In 1:10 pBP:cement samples, % recovery in water extraction varies between 45 and 55% over the period from 12 h to 90 days, but dips to a low of 9% at 1 year. Again, effective immobilization is not achieved at any concentration or any time of cure.

4. EPMA shows inhomogeneous distribution of Br at the 10 um level. There are distinct Br-rich phases, presumably the Ca salt.

5. XRD shows new peaks, probably the Ca salt of pBP.

6. XRD shows significantly decreased crystallinity.

7. The presence of pBP allows the basic reaction chemistry of setting cement to proceed.

GENERAL CONCLUSIONS

Clearly neither the phenols used in this study nor ethylene glycol is effectively immobilized by cement alone at any concentration studied. We assume that this will be the case also with other relatively water-soluble organics. The only evidence for reaction between the organics and the fixing medium is salt formation. Indeed, when salt formation occurs, as in the case of the phenols, the organic becomes more water soluble and more easily extractible from the solidified matrix. There appear to be several distinguishable environments for the organics in the cement matrix:

(1) a separate microscopically distinguishable phase, as with the Ca salt of pBP; as such it is easily extractible;
(2) an environment from which the organic is rather easily extracted by water but not by less polar solvents; probably involving hydrogen bonding by the organic hydroxy groups in interlayer spaces of CSH gel;
(3) an environment in which the organic is quite loosely bound and easily extracted by any solvent in which it is moderately soluble; this environment may also involve the CSH phase.

The idea that there are a definite number of binding sites in the cement matrix at which the organic may be effectively immobilized is not borne out by our work. Even at the lowest concentrations of organics in the cement matrix, water efficiently extracts the organics.

The cement matrix is affected in dramatic ways by the presence of organics. Presumably also the ability of the matrix to contain other wastes, such as metal ions, will be affected by the changes induced by the presence of organics. The matrix changes are dependent on the nature and the concentration of the organic. The changes in easily observable or measurable properties of the matrix are greatest with EG; less with pCP and least with pBP. At or below a 1:10 ratio of organic to cement the effects of all three organics on the easily measurable properties of the matrix are rather minor. All give homogeneous matrices which look like set cement; set times are affected to a significant degree by EG but not much by pCP and pBP; compressive strengths at 28 days are comparable to that of cement pastes without additives. Nevertheless, while SEM, TEM and XRD indicate that some cement hydration reactions are taking place in the same way that they do in the absence of the organic, the situation is much more complex. New phases are formed; the usual phases appear to undergo solid solution formation giving shifted XRD peaks; new morphologies appear with increasing frequency with increasing concentration of organic. Although the changes can be documented, the effects of such changes on some of the measurable properties, particulatly compressive strength, are minor. The most inportant point will be whether the changes affect the immobilizing ability of the matrix toward a variety of wastes. Some information of the latter kind should be available from the WES project, with which we are cooperating. The results of our participation in that work will be reported as Phase 2 of this project.

Nevertheless, additional work needs to be done to bridge the gap between the work done here and field applications of solidification technology. Cementitious solidification/stabilization is most commonly used for immobilization of metal ions. We have shown in preliminary work that Cd in the form of a $Cd(OH)_2$ sludge is effectively immobilized by cement alone, at least at relatively low loadings of the sludge. Success is being judged by the results of TCLP extraction. What now needs to be done is to investigate the effectiveness of immobilization, as measured by TCLP, as various such metal-containing wastes are solidified, increasing the waste-to-cement ratios gradually until failure occurs. At the same time increasing amounts of organic interferences should be added. In addition to monitoring metal and organic concentration in TCLP leachates, the matrix changes should be monitored using the techniques developed in this study. We can thus have a thorough characterization of the matrix in cases where immobilization is effective, and can watch changes in the matrix which occur as we approach failure of the system. We could thereby identify what changes are associated with decreasing (or increasing) effectiveness of immobilization.

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